

NOVEL MECHANISTIC PATHWAYS IN ORGANIC TRANSFORMATIONS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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CHM-1981-D-KHC-

to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
AUGUST, 1981

DEDICATION

A decorative element consisting of three vertical lines of varying lengths, positioned to the right of the word 'DEDICATION'.

Dedicated to the Sacred Memory
of
my beloved departed friend
Late Sri C. P. K. Reddy
and
To my parents


"By its nature, a mechanism is an interpretation of a reaction or process, and as such it depends largely on the eyes of the beholder."

--- Jay K. Kochi

STATEMENT

I hereby declare that the matter embodied in this thesis, "NOVEL MECHANISTIC PATHWAYS ⁰²⁸⁵² IN ORGANIC TRANSFORMATIONS" is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor P.R. Singh.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



JITENDER MOHAN KHURANA

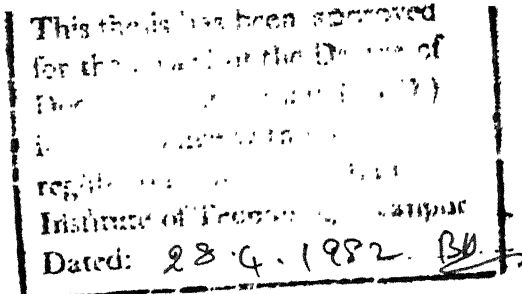
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CERTIFICATE

Certified that the work "NOVEL MECHANISTIC PATHWAYS
IN ORGANIC TRANSFORMATIONS" has been carried out by
Mr. Jitender Mohan Khurana under my supervision and the
same has not been submitted elsewhere for a degree.

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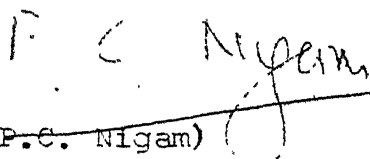
CERTIFICATE OF COURSE WORK

This is to certify that Mr. Jitender Mohan Khurana has satisfactorily completed all the course requirements for the Ph.D. programme in Chemistry. The courses include:

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Chm 501 Advanced Organic Chemistry I
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Chm 521 Chemical Binding
Chm 523 Chemical Thermodynamics
Chm 524 Physical Methods in Organic Chemistry
Chm 541 Advanced Inorganic Chemistry I
Chm 600 Basic Course in Mathematics II
Chm 619 Frontier Topics in Organic Chemistry
Chm 800 General Seminar
Chm 801 Special Graduate Seminar
Chm 900 Research

Mr. Jitender Mohan Khurana has successfully completed his Ph.D. written and oral qualifying examinations and was admitted to the candidacy of the Ph.D. degree in August 1976.


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The pleasant cooperation of my colleagues Dr. H.K. Singh Dr. (Mrs.) Jyoti Singh, Mrs. Ameeta Agarwal, Mr. N. Govindraj, Mr. K.C. Khemani, Mr. Anil Kumar, Mr. Ambrish K. Singh and Mr. O.P. Kureel is gratefully appreciated. I am thankful to all my friends particularly Dr. M.M. Mehrotra, Dr. I.A.K. Reddy,

Mr. S. Dinesh Kumar, Miss Pratibha Chopra, Mr. Raaj Kumar, Mr. Muddukrishna, Dr. P. Subramanian, Mr. M. Amin Khan for making my stay pleasant at this institute. The sprightly sense of humour and undiluted hospitality of Mr. Rajeev Sharma is greatly appreciated. The highly congenial atmosphere and co-operation extended by research scholars in the Core Building is heartily appreciated.

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Finally, all my efforts would have been futile without the loving patronage of the members of my family: my brother-in-law, Mr. K.L. Grover, my brothers Mr. K.K. Khurana and

Mr. H.K. Khurana, sisters Mrs. Santosh Grover and Dr. (Mrs.) Bhavna Khanna and Bhabhi Mrs. Poonam Khurana. I feel short of words to express my gratitude to my nephew Naveen Grover and niece Gitanjali Grover who have silently endured my absence from home during the last few years.

My thanks are due to the authorities of the Indian Institute of Technology, Kanpur and the Council of Scientific & Industrial Research, New Delhi for financial support.

Jitender Mohan Khurana

PREFACE

Organic electron transfer reactions, the chemistry of radical-anion intermediates, and the role of metal ions and metal complexes in various organic transformations are some of the most vigorously pursued areas of current research interest. Many reactions which formally appeared to proceed by nucleophilic displacement or other ionic pathways have been conclusively proved in recent years to involve electron transfer free radical mechanisms. Reports during the last few years, particularly from the laboratories of Professors J.F. Bunnett, E.C. Ashby, J.F. Garst, J.K. Kochi, N. Kornblum, G.A. Russell and G.D. Sargent have added newer dimensions to the developing areas of electron transfer reactions and metal catalysis in organic chemistry. A new mechanistic class of reactions symbolized by $S_{RN}1$ has emerged. A clearer distinction between closely related processes such as atom transfer, electron transfer and oxidative addition in the reduction of organic halides by metallic species has begun to be made.

This thesis, entitled, "Novel Mechanistic Pathways in Organic Transformations" presents novel mechanistic interpretations on the (i) reduction of benzylic halides with lithium aluminium hydride, (ii) reductive cyclization of Z-2-chlorostilbene to phenanthrene with lithium aluminium hydride, (iii) isomerization of Z-stilbene to E-stilbene in the presence of

lithium aluminium hydride, (iv) reduction of benzylic halides with sodium dithionite, (v) reduction and dimethylamination of benzylic halides in the presence of cobaltous chloride or ferrous oxalate in dimethylformamide medium, and (vi) role of cobaltous and cobaltic species as catalysts in the reactions of Grignard reagents with alkyl and aryl halides.

The subject matter of the thesis has been divided into six chapters. The first chapter deals with a general review on "Electron Transfer Reactions and Radical-Anion Intermediates" based on the existing literature. Each of the Chapters II through V has been further sub-divided into sections on (1) Abstract, (2) Introduction, (3) Results and Discussion, (4) Experimental, and (5) References. Introduction to each chapter covers a brief literature survey considered appropriate for the chapter. Sequential numbering of Schemes, equations, tables, figures, structures, and references has been repeated in every chapter.

Chapter II highlights the role of lithium aluminium hydride as an electron donor in the reductions of 9-chloromethylantracene, benzhydryl chloride, 9-bromofluorene and Z-2-chlorostilbene as also in the isomerization of Z-stilbene to E-stilbene.

Studies on the sodium dithionite reduction of a few benzylic halides described in Chapter III indicate the intervention of sulfur dioxide radical-anion as the effective

reducing agent which governs the formation of a variety of products in these reactions.

Roles of Co(II) as an outer sphere electron donor reagent in the reduction of benzylic halides, Fe(II) in the non-radical, reductive dimerization of alkyl halides involving an oxidative addition process, and dimethylformamide in the nucleophilic displacement and dimethylamination processes are discussed in Chapter IV.

In Chapter V, the catalytic actions of Co(II) and Co(III) in the reactions of Grignard reagents with alkyl and aryl halides have been examined. Possible intervention of the supernucleophile, Co(I) species arising from the electron transfer reduction of Co(II) or Co(III) with Grignard reagents has been tentatively suggested but the effectiveness of metallic cobalt favourably considered in the literature as the 'active catalyst' in these reactions has not been ruled out.

A summary of the main results and conclusions constitutes the subject matter of Chapter VI.

A part of the work described in the thesis has been summarized in the undermentioned papers, some of which have also been discussed at national and international conferences.

- (1) F.R. Singh, Alok Nigam and J.M. Khurana, "Reduction of Z-2-chlorostilbene with lithium aluminium hydride: Evidence for an electron transfer radical mechanism," Tetrahedron Letters, 4753 (1980).

- (2) F.R. Singh, J.M. Khurana and Alok Nigam
"Novel electron transfer mechanism in lithium
alanate reduction of benzylic halides"
Tetrahedron Letters, 2901 (1981).
- (3) F.R. Singh, J.M. Khurana and Alok Nigam
"Novel electron transfer mechanism in LiAlH_4
reduction of benzylic halides"
Handbook, Fifth National Symposium on Organic
Chemistry, Calcutta, India, March, 1981,
Paper No. F18, p. 30.
- (4) P.R. Singh, J.M. Khurana and H.K. Singh
"Radicals in the reaction of organic halides
with Grignard reagents in the absence and
presence of cobalt catalysts"
Handbook, Second International Symposium
on Organic Free Radicals, Aix-en-Provence,
France, July, 1977, p. 149.

It is suggested that the importance of mechanistic studies on possible electron transfer reactions and metal catalysis in organic chemistry may be much more than previously ever thought.

The writing of this thesis has been an intellectually stimulating exercise and therefore, a labor of joy.

CONTENTS

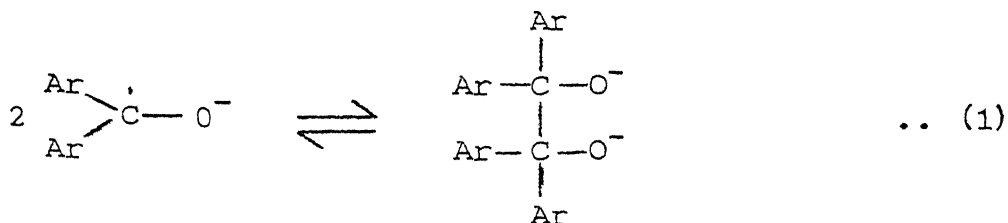
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CHAPTER I

ELECTRON TRANSFER REACTIONS AND RADICAL-ANION INTERMEDIATES

I.1 Introduction

Processes involving transfer of an electron from one reactant to another, giving rise to radical-anion intermediates, in organic reactions have been known for over a century. Although the first report on radical-anions by Berthelot¹ in 1867 went unacclaimed for a long time, the observations made by Bechman and Paul² on the existence of these species during the reaction of sodium with benzophenone under nitrogen atmosphere set forth the development of a new field of chemistry based on radical-anion intermediates. The intense blue coloration in this reaction was attributed to the formation of the radical-anion of benzophenone. The free radical nature of metal-ketyls was established by subsequent investigations.³⁻¹⁰ That the ketyl radical is in equilibrium with the corresponding diamagnetic pinacolate (Eq. 1), was indicated by magnetic susceptibility measurements.^{7,8,10}



Kenner^{11a} suggested in 1945 that organic reactivity should be recognised in terms of oxidation and reduction processes. The statement made by him^{11b} that "radicals rather than ions are produced more frequently than is usually realized" was not given due attention until about fifteen years back when Professors G.A. Russell, N. Kornblum and J.F. Bunnett provided experimental proofs in favor of processes involving electron transfer, thus establishing the intermediacy of radical-anions in several types of reactions. Since then pioneering researches of Professors M. Szwarc, G.D. Sargent, J.K. Kochi, S. Bank, J.F. Garst, R.O.C. Norman, E.C. Ashby, A.J. Birch, H.O. House, J.A. Wolfe, J.A. Marshall, R.A. Rossi and several other eminent scientists have contributed to the development of this area of immense chemical interest.

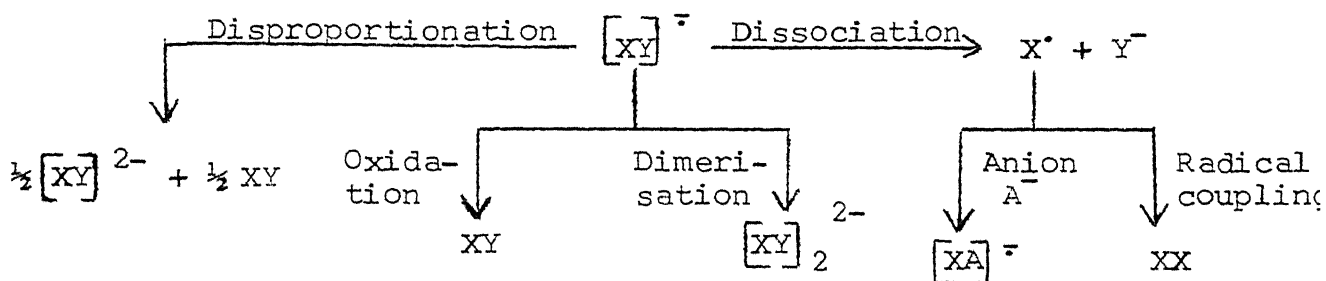
A chemical, electrolytic or photolytic single electron reduction of a suitable molecule may lead to the formation of a radical-anion (Eq. 2):



The new odd electron species with an overall negative charge, characteristic of an anion, may undergo various types of

reactions as outlined in Scheme I.1:

SCHEME I.1



Production of radical-anions and their reactions have been extensively reviewed.¹²⁻²⁴ Recently, ESR,²⁵⁻²⁸ UV^{29,30} and CIDNP³¹ studies have gained popularity as important tools for the investigation of radical-anions.

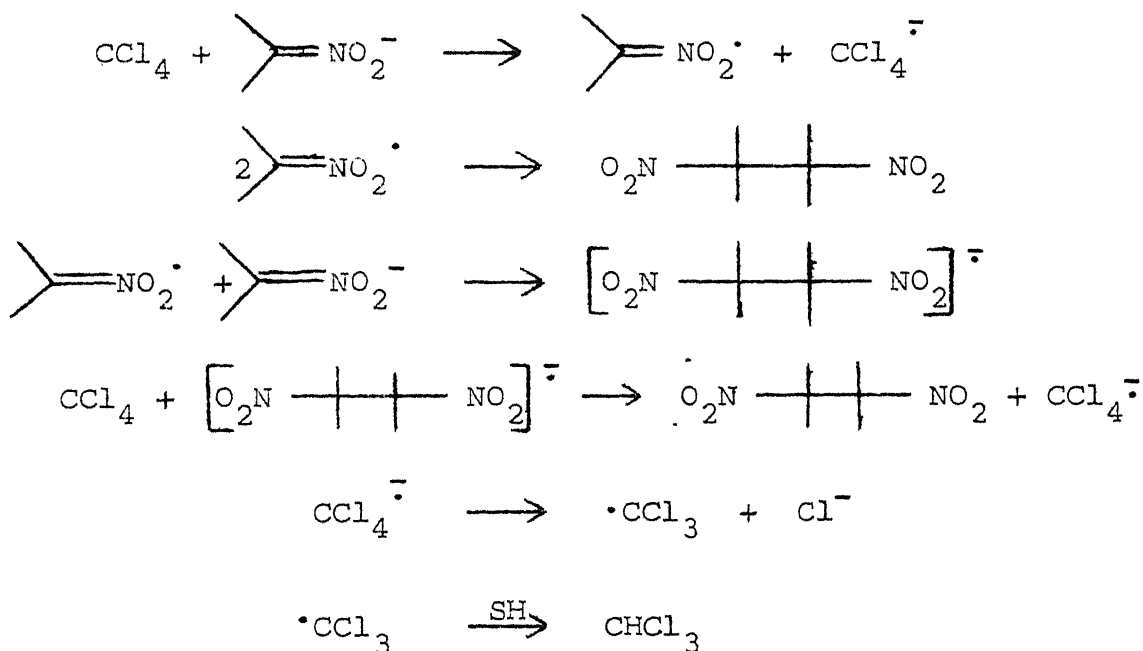
A wide-variety of chemical species are known to act as donors in electron transfer reactions. For example, metals,³²⁻⁴¹ organometallic reagents and carbanions,^{31a,42-52} anions,⁵³⁻⁵⁹ metals in their lower oxidation states,⁵⁹⁻⁶⁷ Lewis bases⁶⁸⁻⁷⁴ and alkyl radicals^{67,75-78} are known to transfer electrons to appropriate substrates. Carbonium ions,⁷⁹⁻⁸¹ metal ions in their higher oxidation states,^{62,82-84} aromatic hydrocarbons,^{33b,85-91} molecules with electronegative substituents⁹²⁻⁹⁴ and radicals^{35,95,96} etc. accept electrons to produce corresponding radicals, metal ions in lower oxidation states, radical-anions and anions respectively, when energy requirements are satisfactorily met.

I.2 Organic and Inorganic Anions as Electron Donors

Suitable electron acceptors may oxidise anionic species to the corresponding radicals by electron transfer process. Schlenk⁹⁷ reported the formation of benzophenone ketyl arising from the reduction of benzophenone with triphenylmethyl carbanion. This was one of the earliest examples of electron transfer processes. Now, anions such as tert-butoxide, 2,4,6-tri-tert-butylphenoxide and triphenylmethyl carbanion are known to transfer an electron to various substrates.^{14,81,98} Aromatic nitro compounds, when treated with anions,⁹⁹⁻¹⁰² are known to form radical-anions.

A number of oxidising agents have been reported^{99,102} to react with carbanions resulting in oxidative dimerisations. For example, carbon tetrachloride brings about the oxidative dimerisation of 2-nitropropanate anion (Scheme I.2):

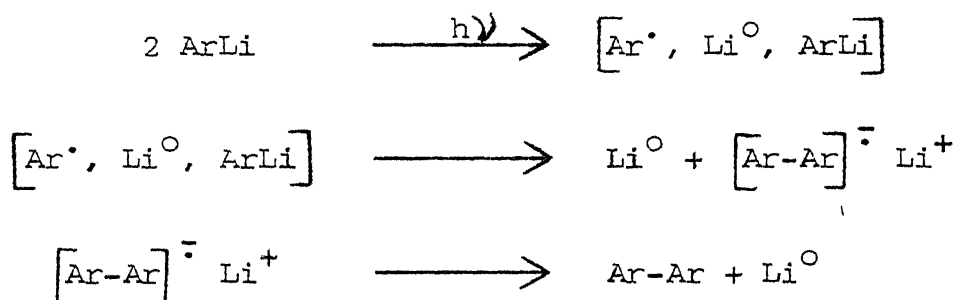
SCHEME I.2



2-Nitropropanate anion¹⁰³ reacts with diaryl iodonium salts by initially donating one electron to the substrate giving cage and escape products of radical intermediates. Reactions involving electron transfer from thiophenoxide^{58a,104-106} and alkoxide¹⁰⁷ anions have also been reported. The electron transfer from a donor reagent is feasible only when the substrate has sufficiently high electron affinity. This explains why butyllithium¹⁰⁸ does not add to tetraphenylethylene or 1,1,3,3-tetraphenylbut-1-ene and also why the reactions of aromatic nitro compounds occur with great ease even with poor donors like alkoxides.¹⁰⁹

Organolithium compounds are known to act as electron donors towards aromatic hydrocarbons,¹¹⁰ oxygen²¹ and peroxides.¹¹¹ van Tamelen¹¹² has observed that photolysis of phenyllithium and α -naphthyllithium in diethyl ether gives biphenyl and 1,1'-binaphthyl respectively, according to Scheme I.3:

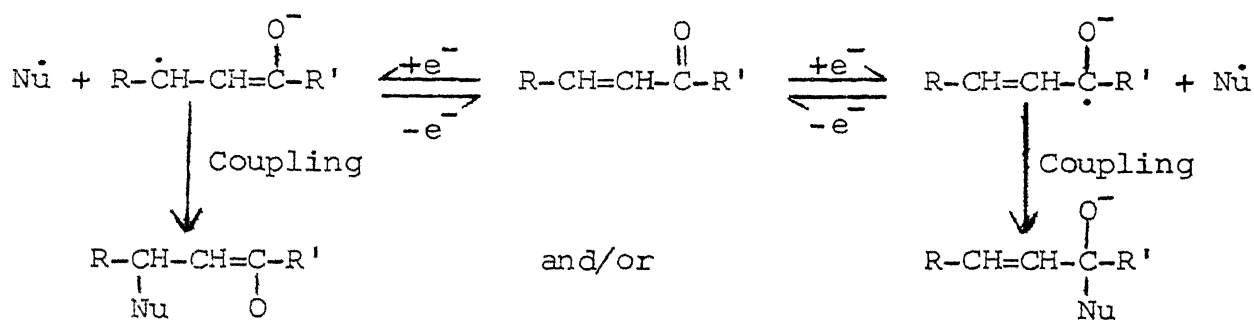
SCHEME I.3



Lithium organocuprates add to unsaturated carbonyl compounds¹¹³ and also react with O₂, PhNO₂ or Cu(II) salts

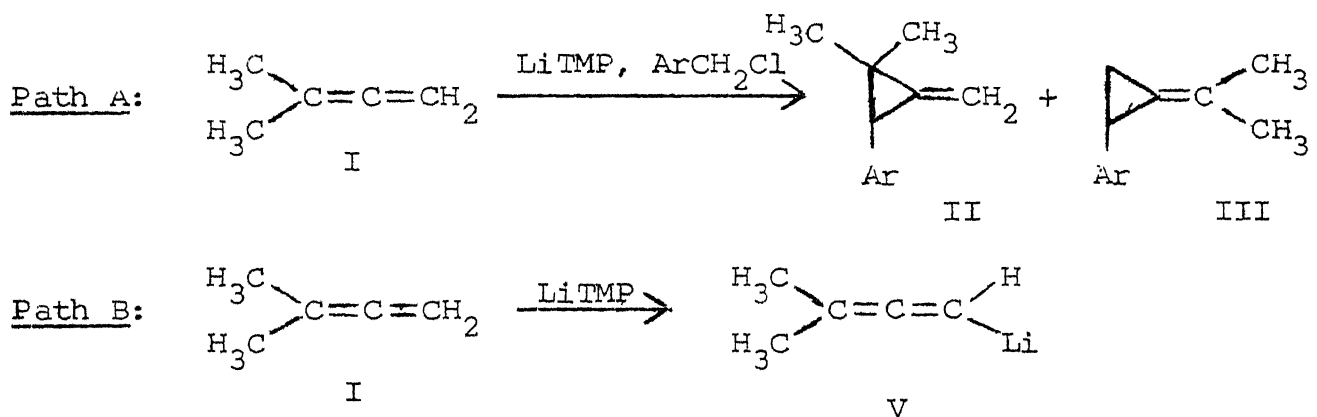
having electrode potentials higher than -1.2 V, by a two step electron transfer process as shown in Scheme I.4:

SCHEME I.4

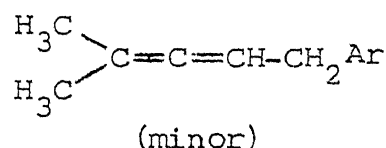
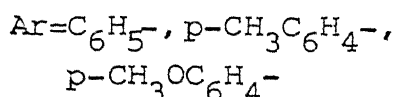
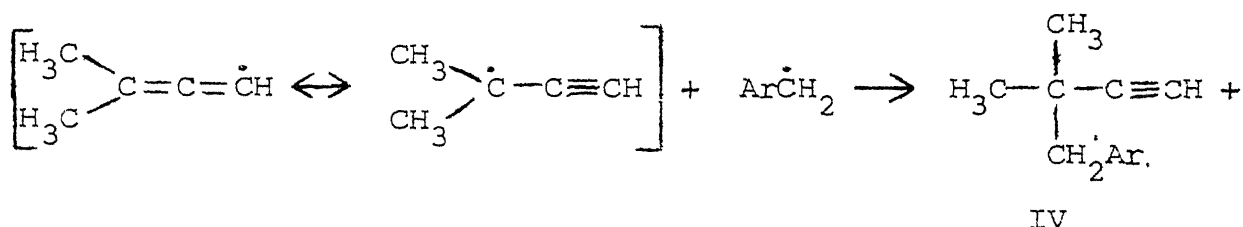
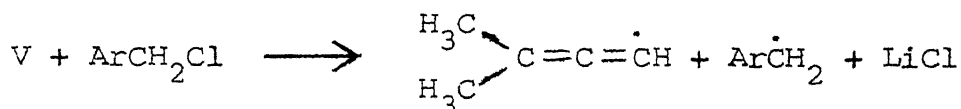


Addition of an ethereal solution of lithium tetramethylpiperidine¹¹⁴ (LiTMP) to a mixture of benzylic chloride and 1,1-dimethylallene (I) yields cyclopropanation products (II) and (III), along with the alkyne (IV). Whereas cyclopropanation products arise from the addition of aryl carbene to allenic double bonds (path A, Scheme I.5), the formation of alkyne can be rationalized in terms of electron transfer as illustrated in path B, Scheme I.5:

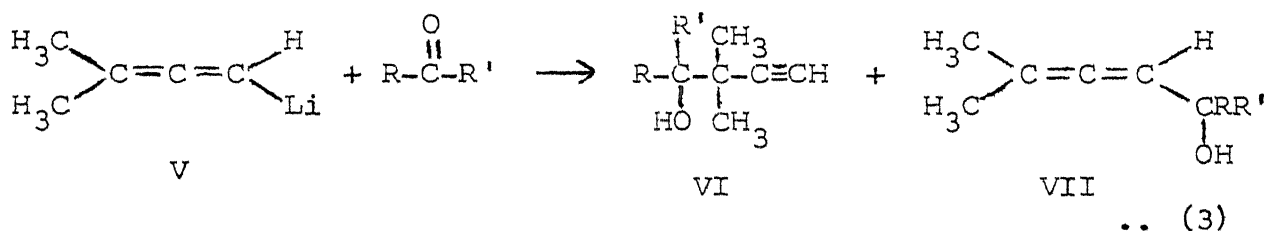
SCHEME I.5



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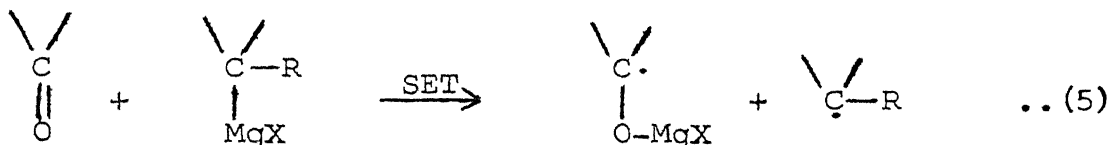
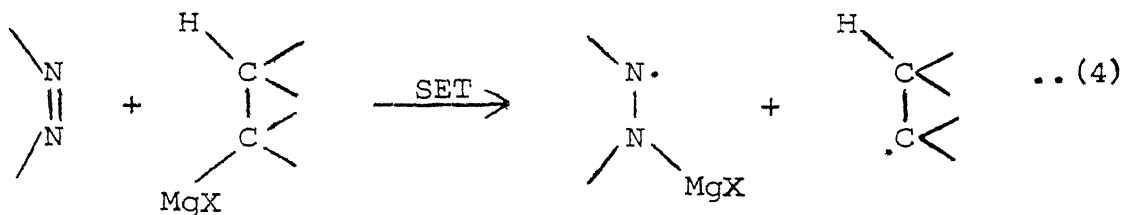


By a similar electron transfer mechanism, anionic species (V) reacts with a ketone¹¹⁵ to form an acetylenic alcohol (VI) and allenic alcohol (VII) as shown in Eq. (3):



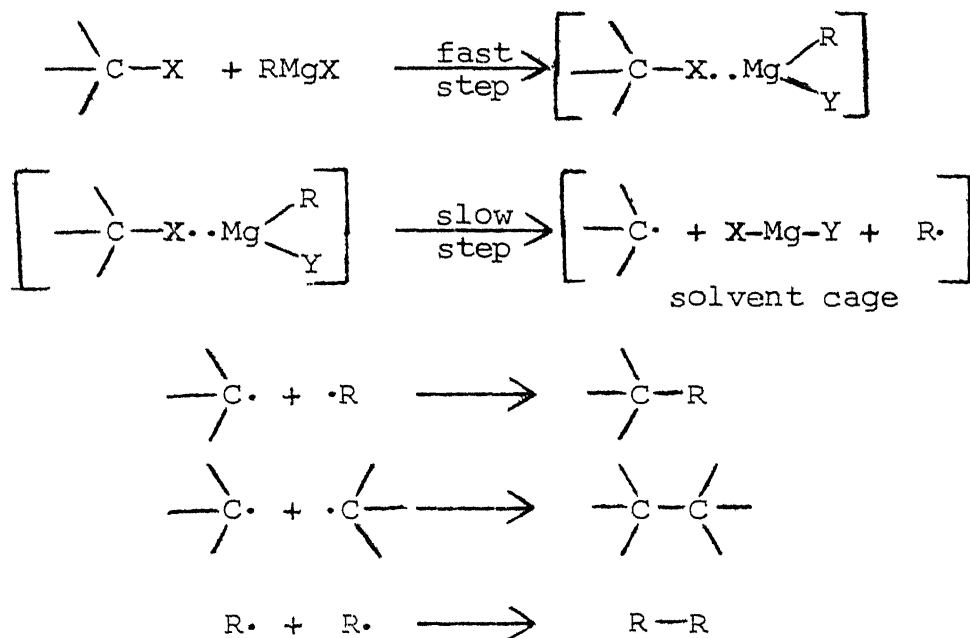
Reactions of Grignard reagents with numerous substrates involve single electron transfer as the first step. Electron transfer from Grignard reagents to oxygen,¹¹⁶ ketones,^{42-44,47} diazonium salts,¹¹⁷ alkyl halides⁵⁰ and non-benzenoid aromatic compounds⁴⁷ have been reported.

Azobenzene and benzophenone¹¹⁸ are reduced by Grignard reagents via single electron transfer as illustrated in Eqs. (4) and (5):



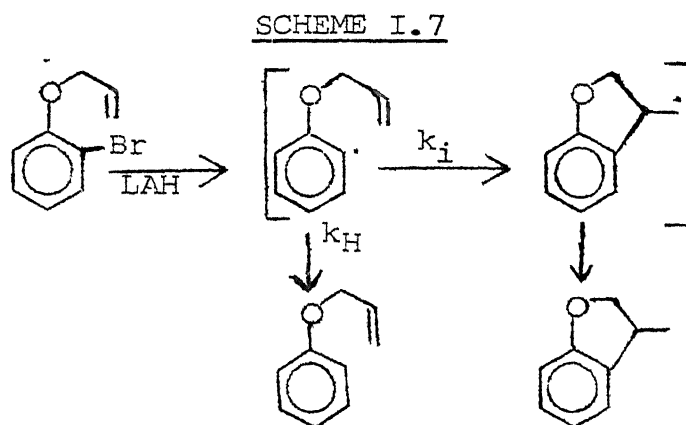
Singh et al.⁵⁰ have proposed electron transfer as the first step in the reaction of Grignard reagent with alkyl halides as shown in Scheme I.6:

SCHEME I.6



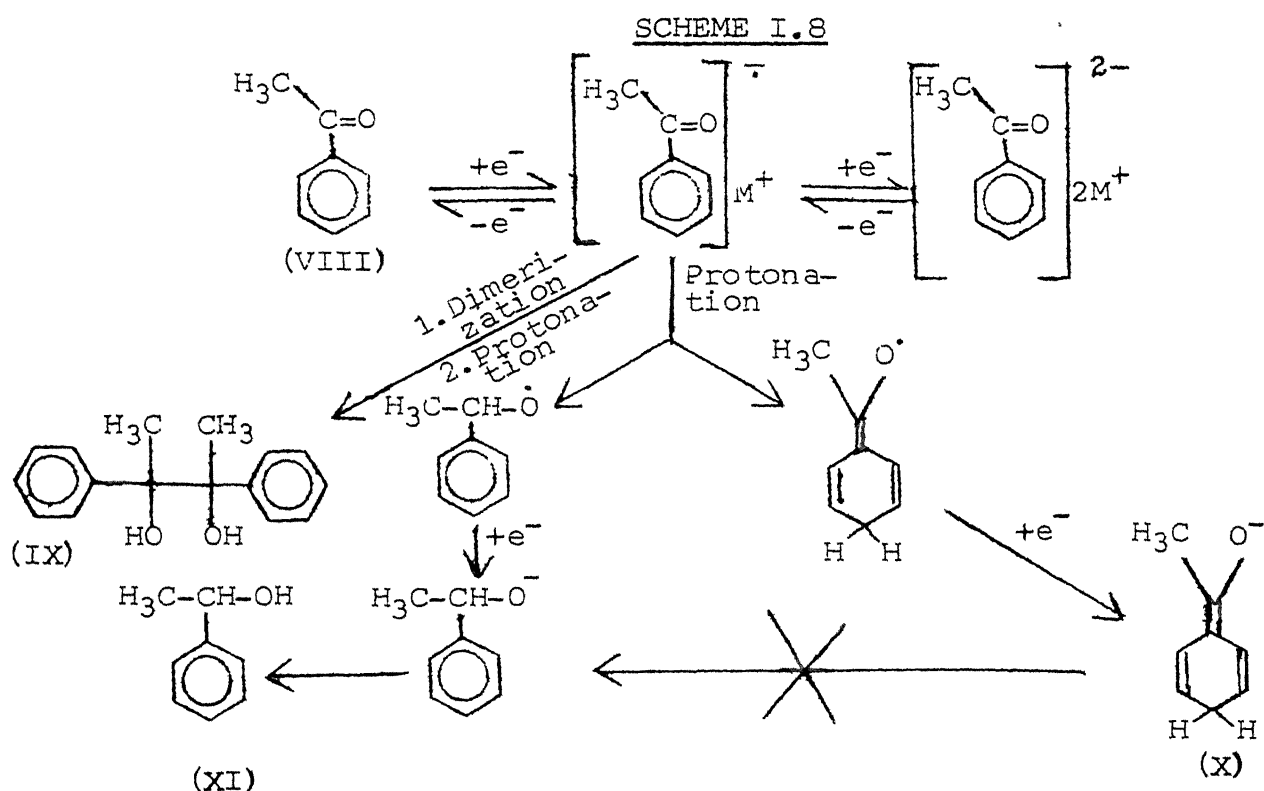
Electron transfer involving lithium aluminium hydride¹¹⁹ (LAH) has also been reported. o-Bromophenyl allyl ether

produces phenyl allyl ether and 3-methyl-2,3-dihydrobenzofuran in which LAH acts not only as a source of electrons but also hydrogen atoms as illustrated in Scheme I.7:

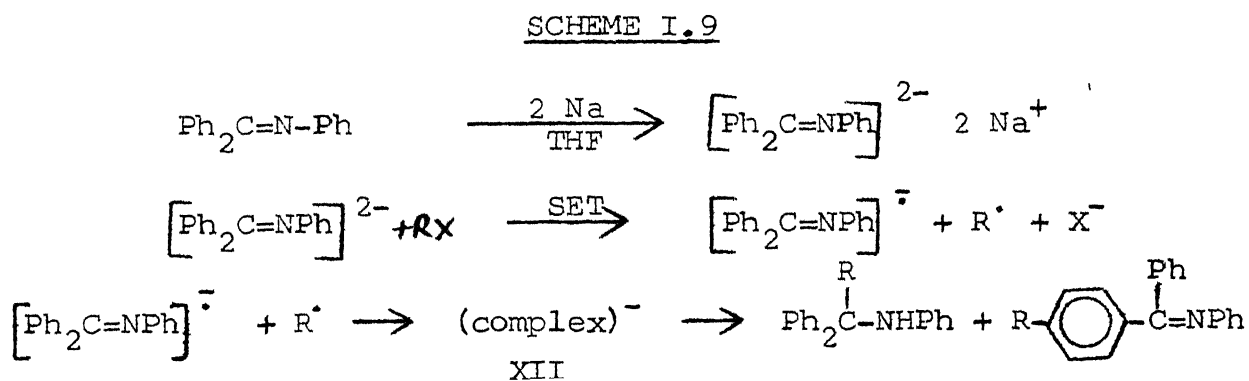


I.3 Generation of Radical-anions Using Metals as Donors

Solutions of alkali metals as well as calcium, magnesium, zinc and iron in liq. ammonia,^{120,121} low molecular weight amines¹²²⁻¹²⁴ or ethers like DME, THF¹²⁵ etc, are known to reduce a wide variety of organic substrates.¹²⁶⁻¹³² The hypothesis^{120a} that dissolving alkali metal reductions are brought about by nascent hydrogen liberated during the reaction of alkali metal and hydroxylic solvent holds no longer. Such reductions are now better understood as internal electrolytic reductions¹³³ in which an electron is transferred from the metal surface or the metal in solution to the organic molecule under consideration. The reduction of acetophenone¹³⁴ (VIII) with lithium and liq. ammonia gives 2,3-diphenylbutane-2,3-diol (IX), 1-(cyclohexa-2,5-dienylidene)enolate (X) and 1-phenethyl alcohol (XI) as shown in Scheme I.8.



Reduction of $-\text{C}=\text{N}-$ bond by alkali metals in protic solvents can produce radical-anions, monomeric and dimeric dianions.^{135,13} The monomeric dianions act as nucleophilic reagents^{135a} and also participate in electron transfer processes.^{135b} This is illustrated by the reaction of benzophenone anil and alkyl halide with Na/THF by a mechanism outlined in Scheme I.9:



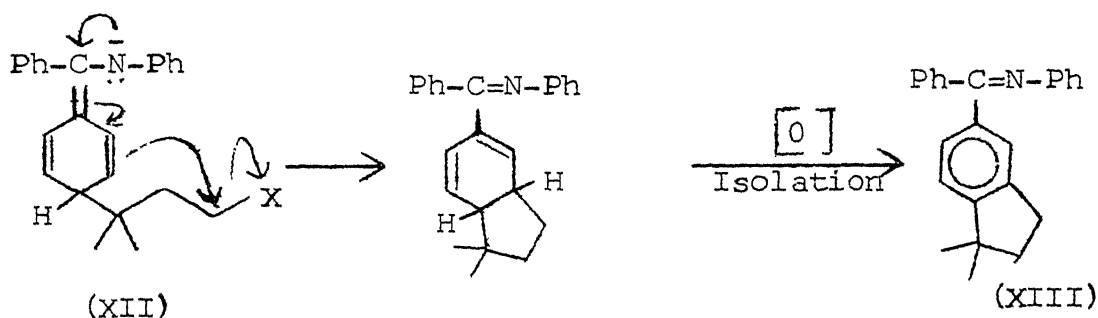
Reaction of Benzyl magnesium chloride with bromobenzene in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$.

To a solution of bromobenzene (1.57 g, 0.01 mol) and $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) in 50 ml of dry THF was added Grignard reagent prepared from benzyl chloride (1.58 g, 0.0125 mol) in dry THF (50 ml) under N_2 atmosphere. The reaction mixture was refluxed for a period of 3 hr after which it was cooled to room temperature and worked up after addition to acidified water. The products were extracted with solvent ether, the ethereal extract washed with water and dried over MgSO_4 (anhyd.). The product mixture after concentration at about 40° was subjected to GLC analysis using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The relative ratios of products in the mixture was found to be diphenylmethane $\sim 3\%$ (0.050 g), bromobenzene $\sim 50\%$ (0.785 g), biphenyl, $\sim 24\%$ (0.185 g) and bibenzyl 0.620 g, by calibration method. GLC analysis at lower temperature also indicated the presence of benzene in small amounts. Correcting the yield of bibenzyl for its formation during the Grignard reagent preparation, i.e. $0.620 - 0.227 = 0.393$ g or $\sim 43\%$ of bibenzyl was formed during the reaction.

Reaction of Benzyl magnesium chloride with bromobenzene in the presence of $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$

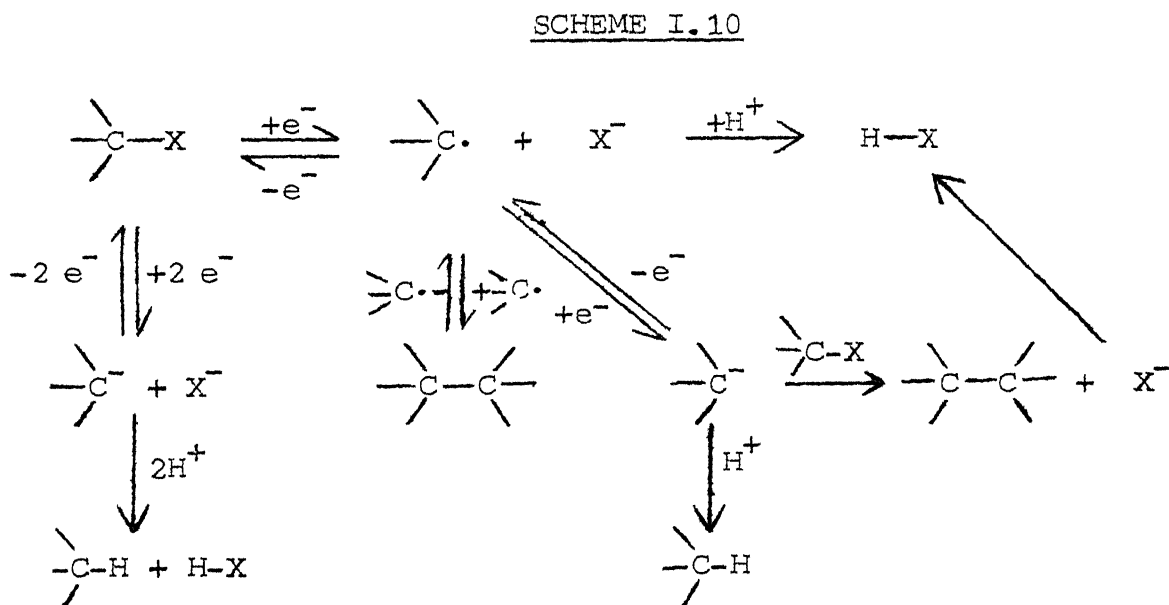
The above reaction was repeated in the same manner except that $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$ (0.286 g, 0.001 mol) was used as catalyst in place of $\text{Co}^{\text{II}}\text{Cl}_2$. Product analyses in the same way showed

If $RX = 1,3\text{-dihalo-3-methylbutane}$, then the complex anion (XII) may partly undergo intramolecular rearrangement giving (XIII) as additional product;



Similar reactions with dianions of thiocarbonyl compounds¹³⁷ and olefins^{138,139} are also known to occur.

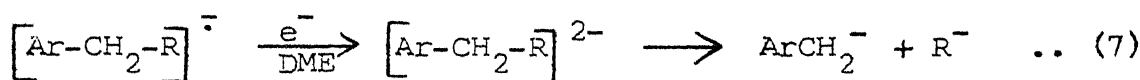
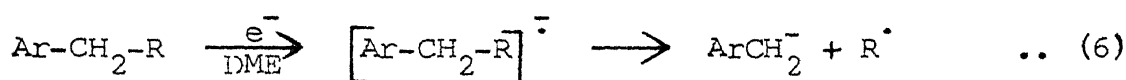
Reductive cleavage of compounds of the type >C-X , where X may be OH, ONO_2 , CR_3 or a halogen, is one of the important reactions of dissolving alkali metal reductions. Mechanistic sequence for such reductions is outlined in Scheme I.10:



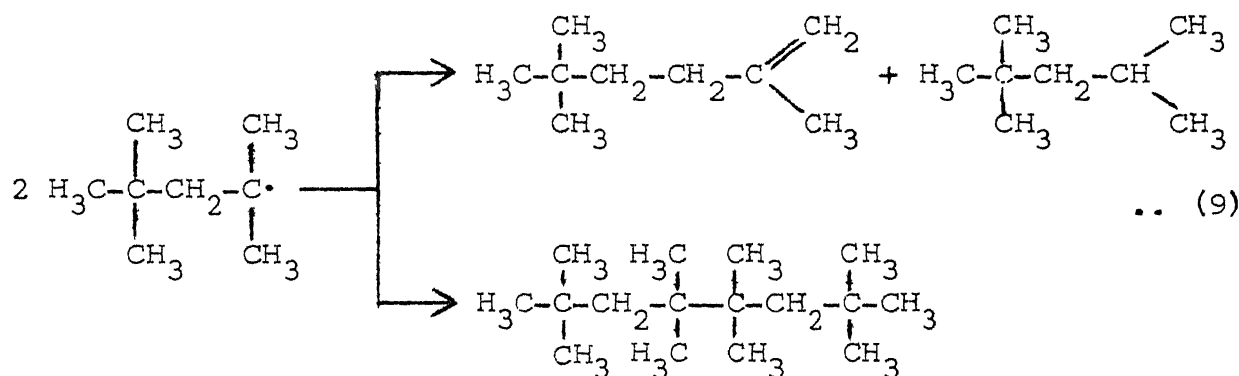
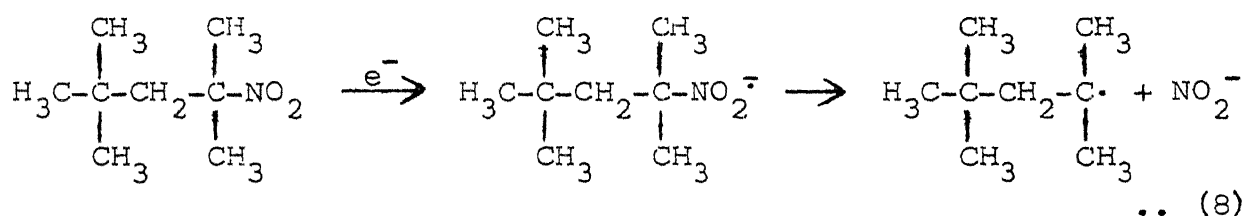
13. (a) R.J. Rogers, H.L. Mitchell, Y. Fujiwara and G.M. Whitesides, *J. Org. Chem.*, 39, 857 (1974).
(b) E.A. Vogler, R.L. Stein and J.M. Wagner, *J. Am. Chem. Soc.*, 100, 3163 (1978).
14. "Methods of Elemento-Organic Chemistry," A. Nesmeyanov and K.A. Kocheshkov (Eds.), North Holland Publishing Co., Amsterdam, Holland, 1967, Vol. 2.
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(b) J.F. Garst in "Free Radicals," J.K. Kochi (Ed.), Wiley-Interscience, New York, 1973, Chapter 9.
(c) H.R. Ward, R.G. Lawler and R.A. Cooper in "Chemically Induced Magnetic Polarization," A.R. Lapley and G.L. Gloss (Eds.), Wiley-Interscience, New York, 1973, Chapter 7 .
16. C. Blomberg, R.M. Salinger and H.S. Mosher, *J. Org. Chem.*, 34, 2385 (1969).
17. H.M. Relles, *J. Org. Chem.*, 34, 3687 (1969).
18. (a) J.J. Eisch and R.L. Harrell, Jr., *J. Organometal. Chem.*, 21, 21 (1970).
(b) R.S. Macomber, *J. Org. Chem.*, 38, 817 (1973).
19. (a) M.E.H. Howden, A. Maerker, J. Burdon and J.D. Roberts, *J. Am. Chem. Soc.*, 88, 1732 (1966).
(b) E.J. Panek and G.M. Whitesides, *J. Am. Chem. Soc.*, 94, 8768 (1972).
(c) J.F. Garst, C.D. Smith and A.C. Farrar, *J. Am. Chem. Soc.*, 94, 7707 (1972).
20. (a) B. Miller, *J. Org. Chem.*, 42, 1402, 1408 (1977).
(b) B. Akermark and A. Ljungqvist, *J. Organometal. Chem.*, 149, 97 (1978).

Studies on the role of cobalt catalysts in the reactions of Grignard reagents with organic halides have been carried out by comparison with the corresponding uncatalyzed reactions. In the reactions of two Grignard reagents (RMgX), namely benzylmagnesium chloride and phenyl magnesium bromide with several organic halides ($\text{R}'\text{Y}$), viz. benzyl chloride, trityl chloride, 9-bromofluorene and bromobenzene catalyzed by Co(II) or Co(III) species, the yields of homo-coupling products R-R and $\text{R}'\text{-R}'$ are found to be enhanced at the expense of the cross-coupling products $\text{R-R}'$. Based on the observations on a large number of reactions, it is concluded that radicals $\text{R}\cdot$ and $\text{R}'\cdot$ are formed in both the uncatalyzed and catalyzed reactions. In the uncatalyzed reactions, these radicals are produced simultaneously permitting both the cross-coupling and homo-coupling reactions to occur side by side. In the cobalt catalyzed reactions, however, radicals $\text{R}\cdot$ are produced (by the Co^{II} or Co^{III} oxidation of the Grignard reagents) first which undergo coupling to give R-R and the radicals $\text{R}'\cdot$ (from the organic halide) are formed in a subsequent step giving ultimately, $\text{R}'\text{-R}'$. Possible intervention of Co^{I} species produced initially by the electron transfer from the carbon-magnesium bond of the Grignard reagent to Co^{II} or Co^{III} , as the active catalyst has been suggested and the role of Co^{I} as a supernucleophile highlighted. A clear distinction between Co^{I} species first suggested in this thesis and metallic cobalt (suggested in the literature earlier) with regard to the actual active catalyst in these reactions has not been possible.

Recent reports on the reductive cleavage of C-O,¹⁴⁰ C-C¹⁴⁰⁻¹⁴² and C-Cl bonds are in conformity with the above mechanism. Schanne¹⁴² has reported the cleavage of benzylic C-C bonds in diarylmethanes and diarylethanes by potassium metal. The reaction path is illustrated by means of Eqs. (6) and (7):



On treatment with sodium,^{129a} 2,4,4-trimethyl-2-nitropentane gives a mixture of hydrocarbons as shown in Eqs. (8) and (9):

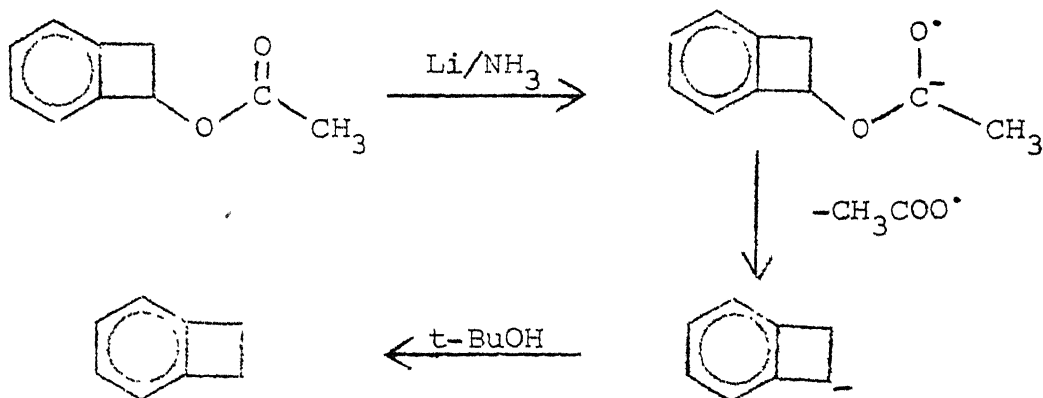


Esters are also known to undergo cleavage via electron transfer. Thus Li/liq. NH₃ affects the cleavage of esters^{100,141a}

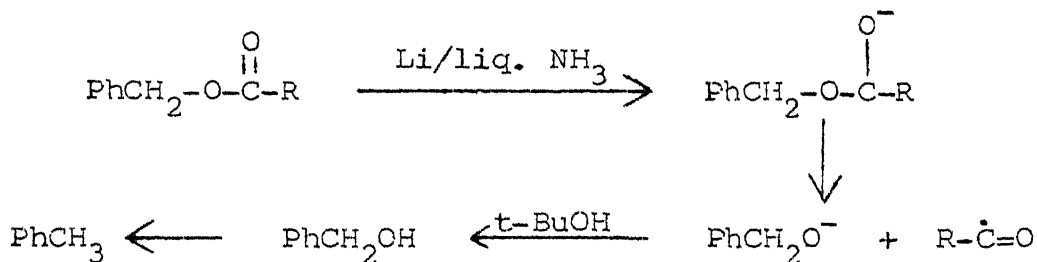
by one of the two pathways outlined in Scheme I.11:

SCHEME I.11

1st Pathway:

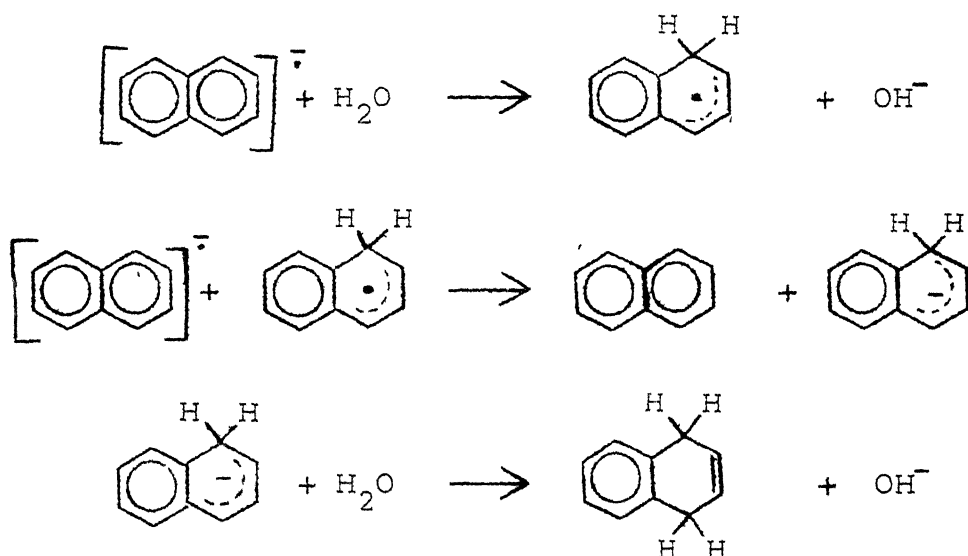


2nd Pathway:

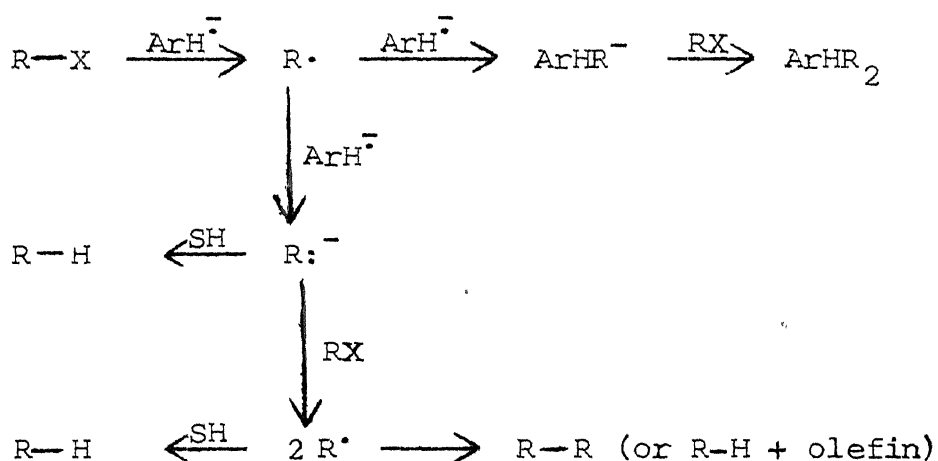


I.4 Reactions of Radical-anions of Aromatic Hydrocarbons

Radical-anions of aromatic hydrocarbons act as potential sources of electrons in numerous electron transfer reactions. These radical-anions can either act as powerful bases and abstract protons from weakly acidic substrates or transfer electron to the appropriate substrate. Sodium naphthalene reacts with water as shown in Scheme I.12:

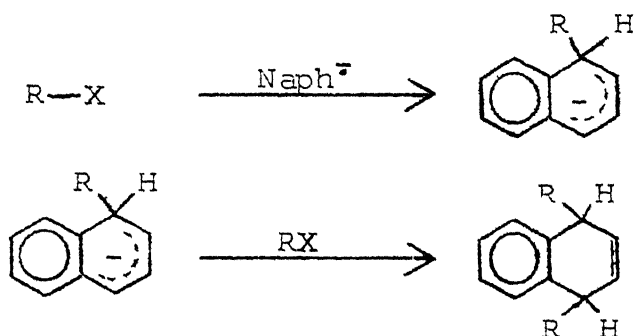
SCHEME I.12

Reactions of alkyl halides with aromatic radical-anions have been thoroughly investigated and reviewed.¹⁴³⁻¹⁴⁵ The general mechanism of these reactions is outlined in Scheme I.13:

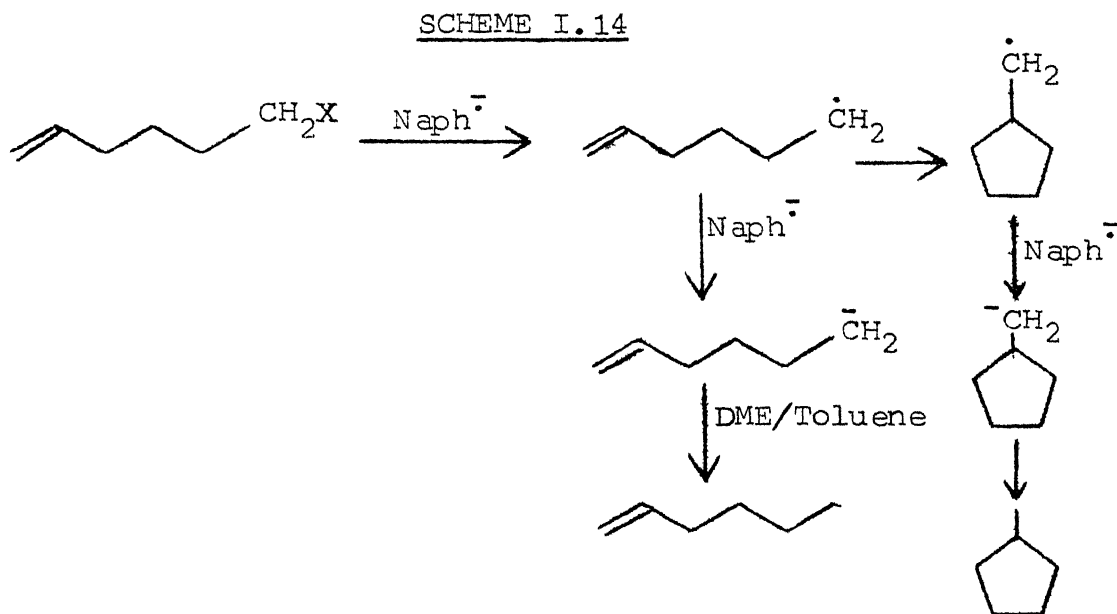
SCHEME I.13

Alkylation of aromatic nucleus proceeds by coupling of alkyl radical with radical-anion giving anion (XIV) which, by

subsequent S_N2 displacement on the alkyl halide, yields dialkylate^{146,147} (XV):

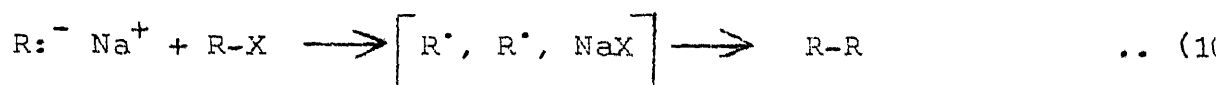


Both, radicals and anions are proposed as intermediates in these reactions.¹⁴⁴ Formation of cyclised product in the reactions of 5-hexenyl halides supports the existence of radical intermediates. But since cyclisation of 5-hexenyl radical is a much faster reaction than hydrogen atom abstraction from solvents like DME or toluene,¹⁴⁸ the formation of more of hexene-1 in this reaction indicates the intermediacy of carb-anions also (Scheme I.14):

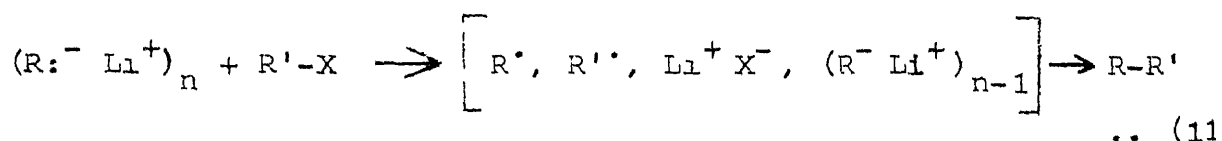


The formation of carbanion intermediates in the reaction of 1,4-diiodobutane and alkyl halides¹⁴⁷ and tetrahydrofurfuryl halides²² with the radical-anions of aromatic hydrocarbons have also been reported.

Reductive dimerisation of alkyl halides probably involve the coupling of geminate radical pairs¹⁴⁷ as shown in Eq. (10)

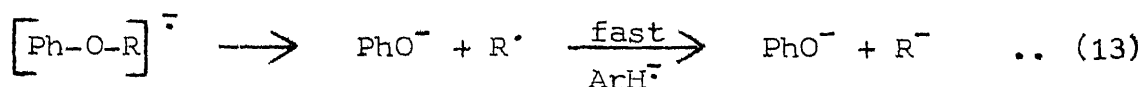
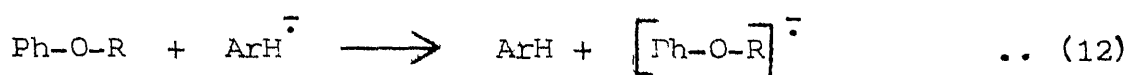


In this respect, the above reaction is parallel to that of alkyl lithiums with alkyl halides, Eq. (11):



The radical pair generated by electron donation from alkyl-lithium in solvent cage may then dimerise, disproportionate or diffuse apart. The intermediate radicals formed in this reaction have been trapped¹⁴⁹ and detected by ESR spectroscopy.¹⁵⁰⁻¹ Dimerisation of alkyl halides have also been observed with metal ions and metal complexes.¹⁵² Cyclopropyl halides are also reduced by alkali metal naphthalenes.¹⁵³

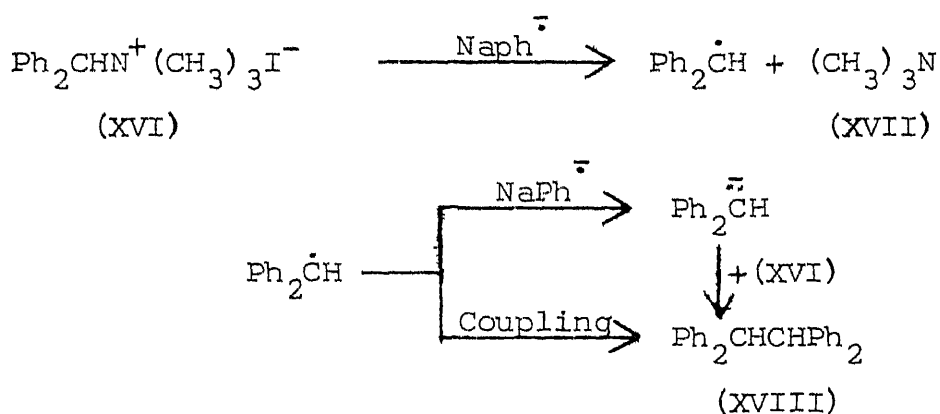
Cleavage of the ether linkage with radical-anions of aromatic-hydrocarbons^{106, 154-157} has also been achieved. The general sequence of steps is believed to be that outlined in Eqs. (12) and (13):



The O-S bond scission in toluene sulfonates^{158,159} and N-S bond scission in N-substituted sulfonamides¹⁶⁰ also follow a sequence of steps similar to that shown by Eqs. (12) and (13).

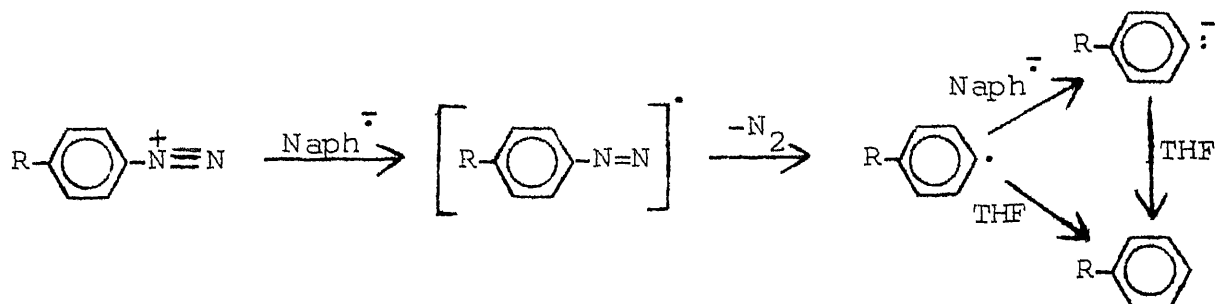
Sodium naphthalene cleaves off a benzylic group from quaternary ammonium salts (XVI)¹⁶¹ to give tertiary amines (XVII) and benzylic dimers (XVIII) as shown in Scheme I.15:

SCHEME I.15



Singh and coworkers¹⁶² have demonstrated that the reactions between sodium naphthalene and arenediazonium salts occur by initial transfer of an electron to the diazonium salt. The steps are outlined in Scheme I.16:

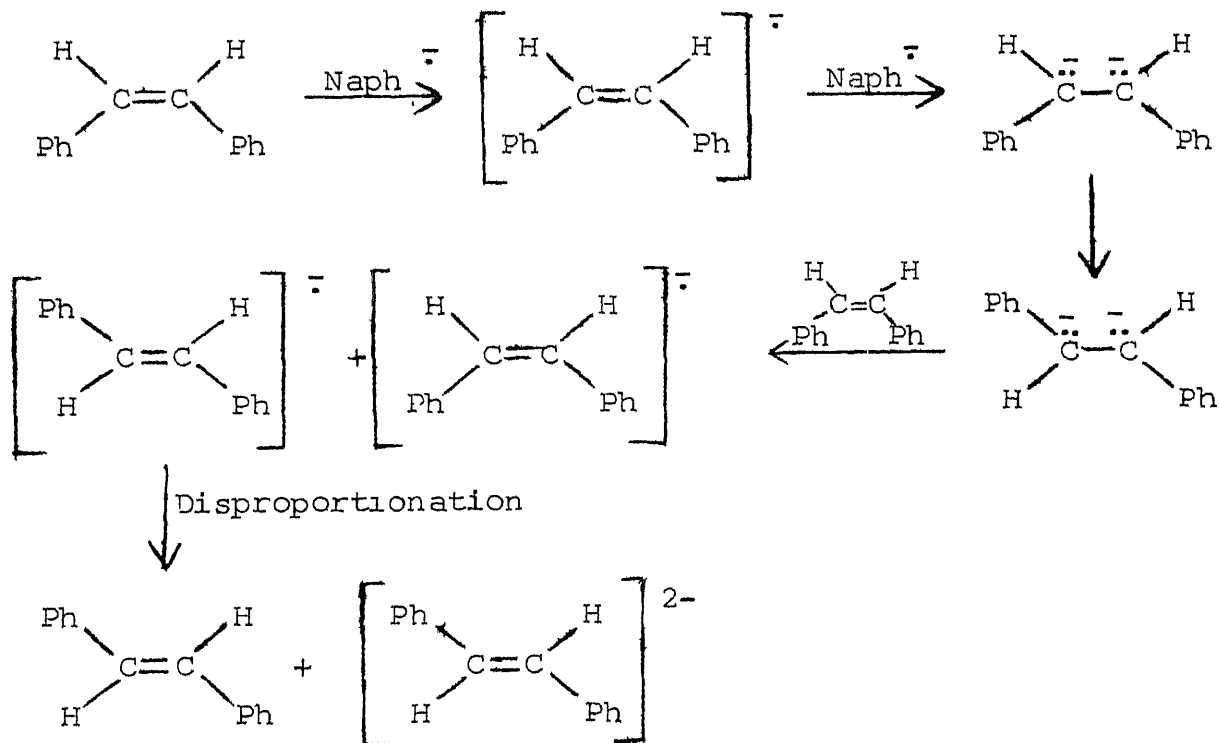
SCHEME I.16



Sodium naphthalene reacts with phenyl acetonitrile^{163,164} to give a mixture of products.

Isomerisation of Z-stilbene to E-stilbene with sodium naphthalene¹⁶⁵ has been postulated to proceed through stilbene dianion (Scheme I.17):

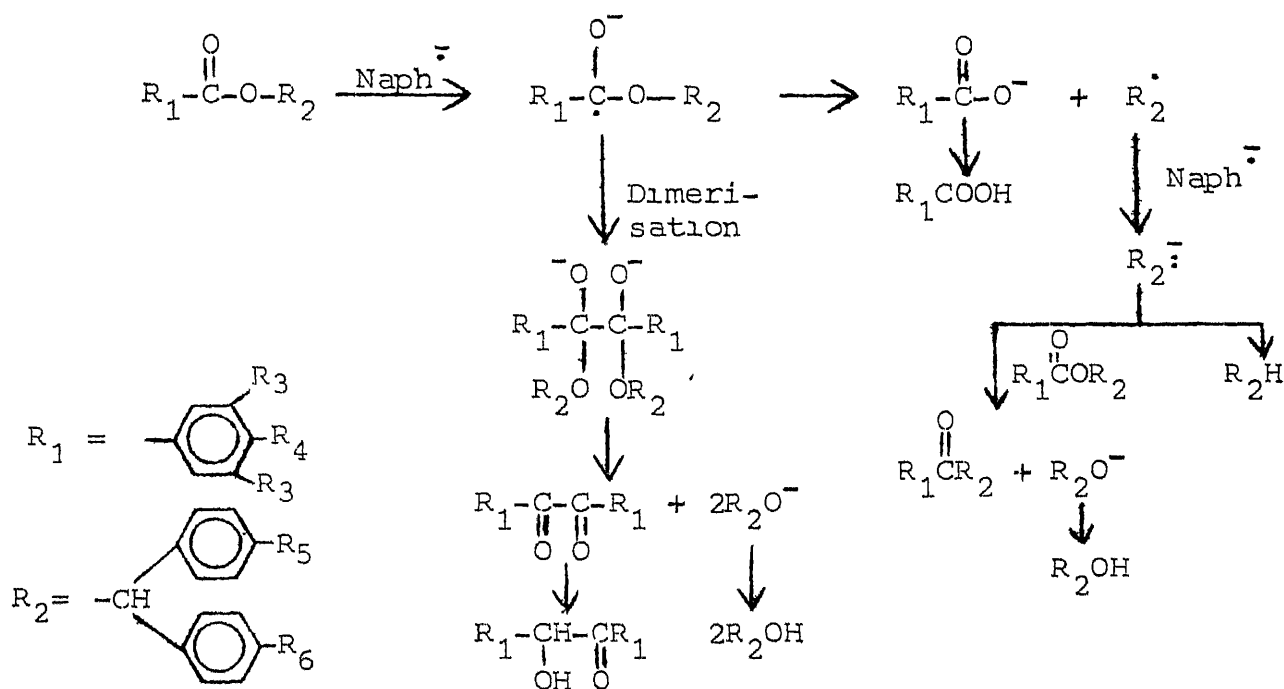
SCHEME I.17



Reductive cleavage of esters has been reported recently.

Substituted benzhydryl benzoates are cleaved by sodium naphthalene as shown in Scheme I.18:

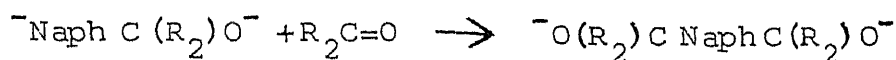
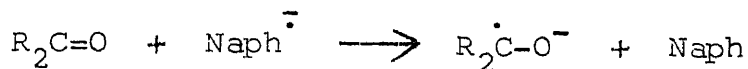
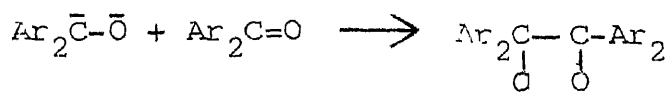
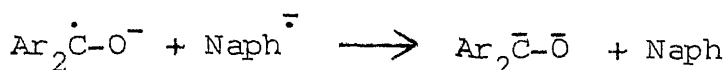
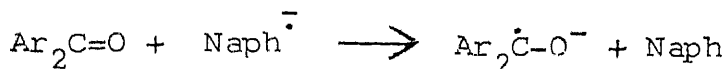
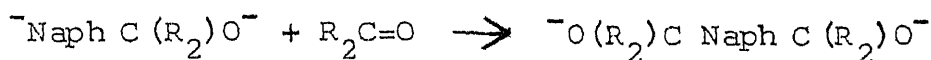
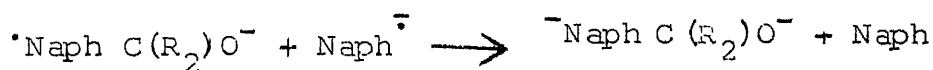
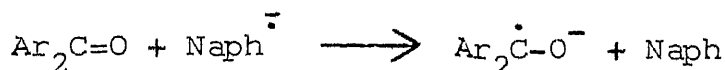
SCHEME I.18



$R_3 = \text{H, OMe}; R_4 = \text{H, OMe, Ph, CN};$

$R_5 = \text{H, Me, Ph}; R_6 = \text{H, Me, Ph}$

Holy and coworkers¹⁶⁸ have reported the reactions of aliphatic and aromatic aldehydes and ketones with sodium naphthalene. Two alternative mechanisms, one involving dianion intermediates and the other free radicals, have been proposed (Scheme I.19):

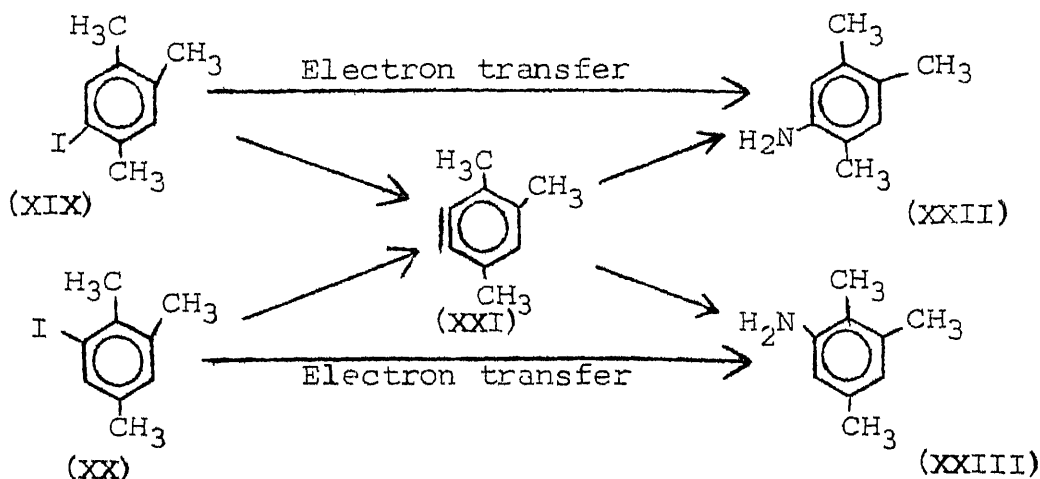
SCHEME I.19(A) Dianion Mechanism(i) Aliphatic carbonyl compounds:(ii) Aromatic carbonyl compounds:(B) Radical Mechanism(i) Aliphatic carbonyl compounds:(ii) Aromatic carbonyl compounds:

Though both these mechanisms account for all the products formed, the actual mechanism of the reactions under study is yet to be established.

Sodium naphthalene reacts with molecular hydrogen¹⁶⁹ to produce sodium hydride in good yield. Naphthalene radical-anions have been successfully used to initiate polymerisation reactions.^{170,171} These are also known to react with sulfur dioxide,¹⁷² carbon dioxide,¹⁷³ alkyl halosilanes¹⁷⁴ and aryl-phosphates.¹⁷⁵ One of the potential uses of sodium naphthalene is in the fixation of molecular nitrogen.¹⁷⁶

I.5 Aromatic Substitution by $S_{RN}1$ Mechanisms

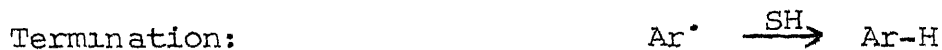
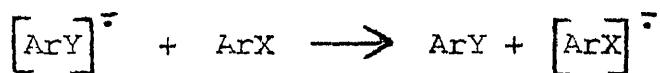
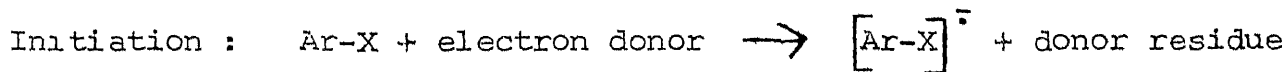
An elegant electron transfer mechanism in 'aromatic nucleophilic substitution' reactions has been demonstrated by Kim and Bunnett.¹⁷⁷ These workers observed that ratio of the two products (XXIII):(XXII) was 0.63 when 5-iodopseudocumene (XIX) was treated with KNH_2 in liq. NH_3 , but the ratio was 5.83 when



6-iodopseudocumene (XX) was used in place of (XIX). These results do not support the intermediacy of aryne (XXI), which should be expected to yield two products in the same ratio irrespective of the position of iodine. Also, catalysis by light and a marked decrease in the amount of the direct substitution product in the presence of tetraphenylhydrazine - a known radical scavenger - were observed. These facts suggest that a significant fraction of the non-rearranging substitution was occurring via a radical chain mechanism, which Kim and Bunnett¹⁷⁷ designated as $S_{RN}1$ (substitution, radical-nucleophilic, unimolecular).

The generalised version of the mechanism is outlined in Scheme I.20. The separate components of this radical-chain sequence have ample precedents and the overall reaction scheme

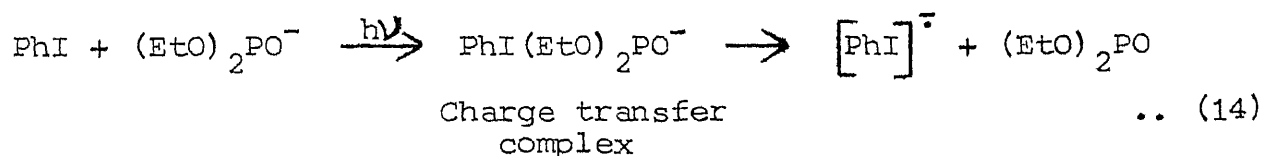
SCHEME I.20



is analogous to that proposed earlier by Kornblum¹⁷⁸ and Russell¹⁷⁹ for reactions of nucleophiles with certain

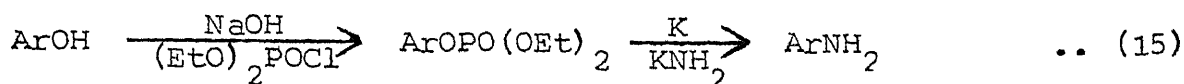
p-nitrobenzyl halides and 2-halo-2-nitropropanes.

Most aromatic $S_{RN}1$ reactions require catalysis by an alkali metal¹⁷⁷ or near-ultraviolet light.¹⁸⁰ Whereas metal initiates the chain by providing solvated electrons, the exact catalytic function of pyrex glass-filtered light is not known with certainty. However, evidence has been presented to support the theory that electron transfer occurs through an intermediate charge-transfer complex.¹⁸¹ These reactions are known as 'photo-stimulated aromatic $S_{RN}1$ reactions'. An example of such reaction is shown in Eq. (14):



For $S_{RN}1$ reactions of amide ion with 5- or 6-iodopseudo-cumene¹⁷⁷ (Scheme I.20) or of pinacolone enolate anion with iodobenzene in DMSO¹⁸² which occur spontaneously in the dark, the mechanism of initiation is not clear. A reasonable possibility¹⁷⁸ is a thermally activated electron transfer from nucleophile to the substrate. Such reactions are known as autoinitiated aromatic $S_{RN}1$ reactions.

The tendency of the groups SPh ,¹⁸³ NMe_3^+ ¹⁸³ and $\text{OPO}(\text{OEt})_2$ ¹⁸³⁻¹⁸⁵ to undergo facile displacement by some other groups via $S_{RN}1$ mechanism has great synthetic importance. For example, Ar-OH can be converted into Ar-NH_2 in very good yields¹⁸⁴ under mild conditions (Eq. 15):

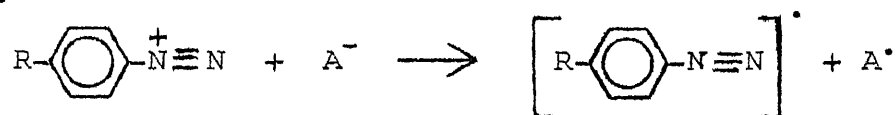


Nucleophiles such as carbanions derived from simple ketones,^{177,180,183,186-191} nitriles,^{185,189,192} 2- and 4-picolines¹⁹³ and conjugated hydrocarbons¹⁸⁷ have received much attention with reference to aromatic $\text{S}_{\text{RN}}1$ reactions. Phosphonates viz. Ph_2P^- ,¹⁹⁴ $(\text{EtO})_2\text{PO}^-$,^{195,196,213,214} $\text{Ph}(\text{BuO})\text{PO}^-$,¹⁹⁷ Ph_2PO^- ,¹⁹⁷ $(\text{EtO})_2\text{P}^-$ ¹⁹⁷ and $(\text{Me}_2\text{N})_2\text{PO}^-$ ¹⁹⁷ have also been used as electron donors. Recently, electron transfer from phenyl selenide,¹⁹⁶ phenyl telluride¹⁹⁸ and N,N-disubstituted amide enolate¹⁹⁹ anions has also been reported.

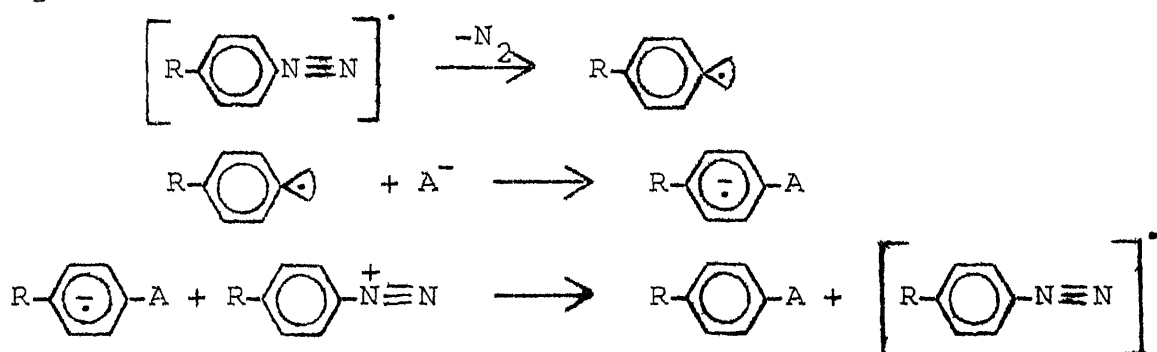
Reactions of arenediazonium salts with different nucleophiles have been studied in our laboratory.^{106,120} The mechanism of the propagation cycle in these reactions is same as that applicable to $\text{S}_{\text{RN}}1$ reactions (Scheme I.21):

SCHEME I.21

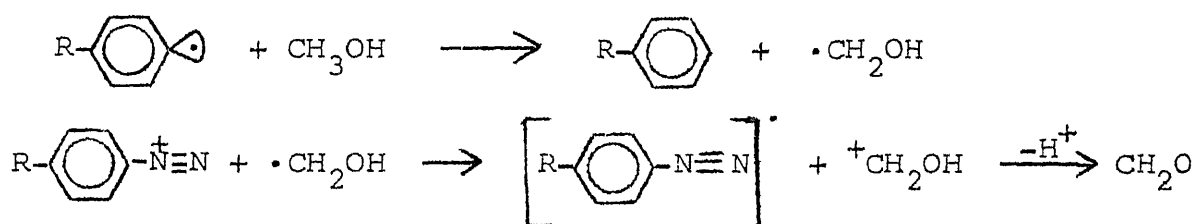
Initiation:



Propagation:

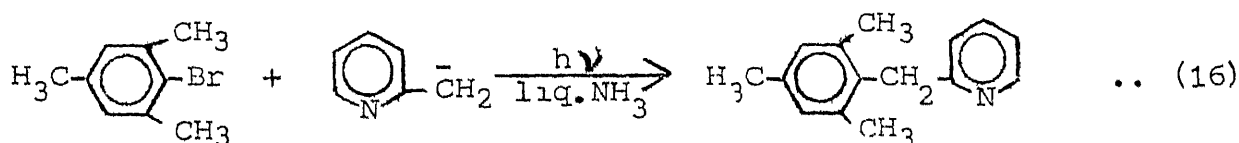


Termination:



where; $\text{A}^- = \text{I}^-, \text{NO}_2^-, \text{PhS}^-$

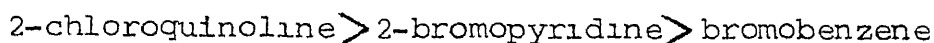
Substituents (other than the nucleofugic group) which appear to interfere with aromatic $\text{S}_{\text{RN}}1$ process are nitro and hydroxyl groups.^{188,192} Steric hindrance has no noticeable effect on aromatic $\text{S}_{\text{RN}}1$ reactions. For example, mesityl bromide affords high yield of substitution product¹⁹³ in the reaction outlined in Eq. (16):



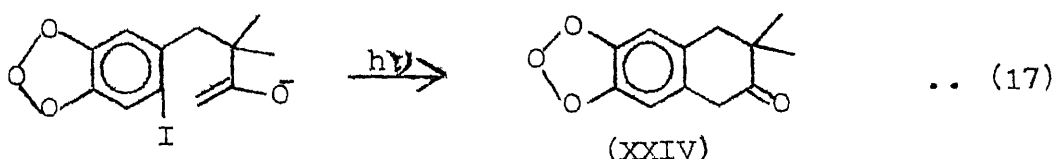
Among sulfanions, arenethiolates²⁰¹⁻²⁰³ and alkane-thiolates^{189,204} have been found to be effective nucleophiles in $\text{S}_{\text{RN}}1$ reactions.

A number of halogenated heterocyclic compounds including 2-, 3- and 4-halopyridines,^{186,192} 2-halopyrimidines,²⁰⁵ 2-chloropyrazine,^{186,205} 2-chloroquinoline,^{190,206,207} halo-isoquinolines^{202,208} and halogen derivatives of thiophene²⁰⁹ are known to undergo $\text{S}_{\text{RN}}1$ reaction in the presence of suitable electron donors. Certain vinylic halides also undergo substitution via the $\text{S}_{\text{RN}}1$ pathway.²¹⁰ That the heteroaromatic halides

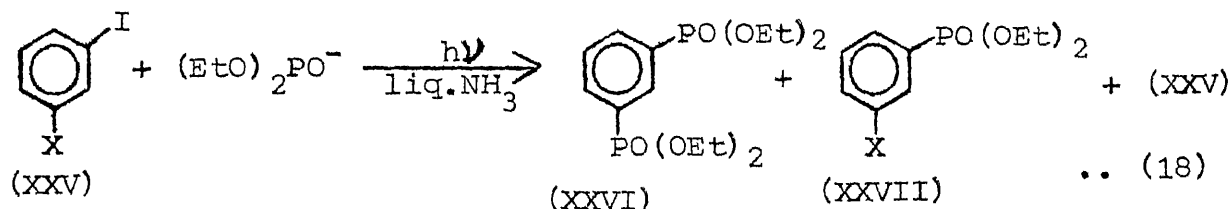
are more reactive than the aromatic halides in $S_{RN}1$ reaction is seen from the following reactivity sequence determined by using potassium acetate as the nucleophile:



Substrates with appropriate structural features may undergo intramolecular $S_{RN}1$ reaction. Thus, the reaction cited in Eq. (17) yields the product (XXIV) in 99% yield.²¹¹



The reactions outlined in Eq. (18) present a very interesting situation.^{203,212-214} Irradiation of m-bromiodobenzene (XXV-C) together with diethylphosphite ion in liq. NH_3 , for example, gave mostly disubstituted product (XXVI) and a small amount of monosubstituted product (XXVII-C) along with unreacted starting material.



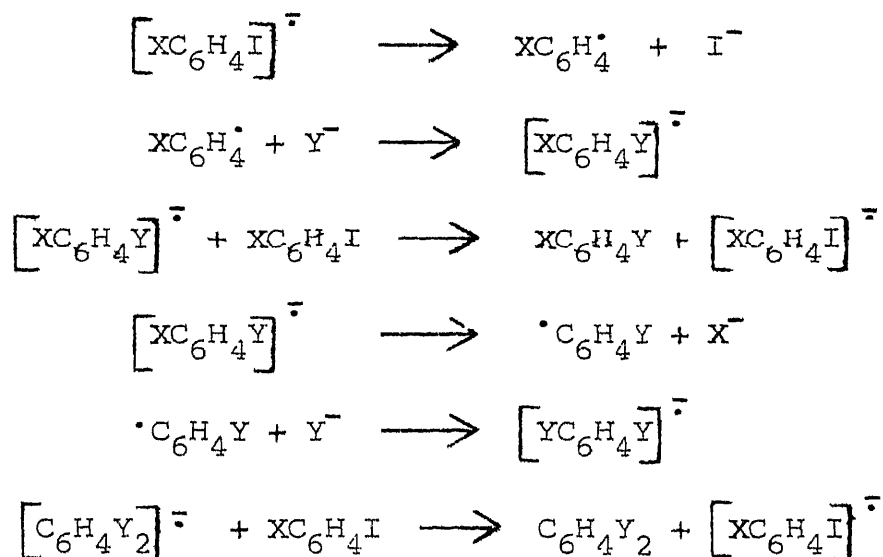
where a, X = F; b, X = Cl;
c, X = Br; d, X = I.

Such a condition might arise if substitution were stepwise and the conversion of (XXVII-C) to (XXVI) were much faster than

that of (XXV-C) to (XXVII-C). However, the transformation of (XXVII-C) to (XXVI) was found to be slower than that of (XXV-C) to (XXVII-C). It is, therefore, clear that (XXVII-C) can not be an intermediate in the conversion of (XXV-C) to (XXVI).

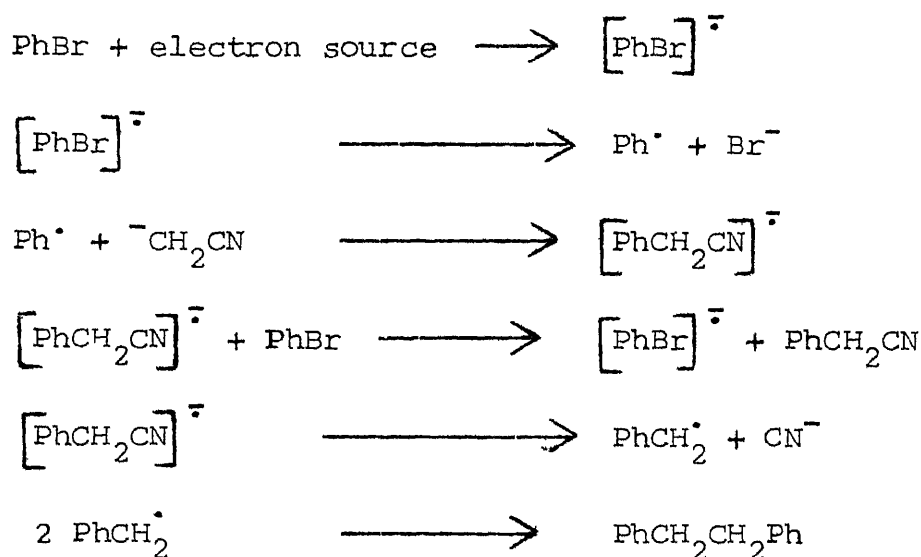
The $S_{RN}1$ mechanism, presented in Scheme I.22, provides a straightforward interpretation of these results:

SCHEME I.22

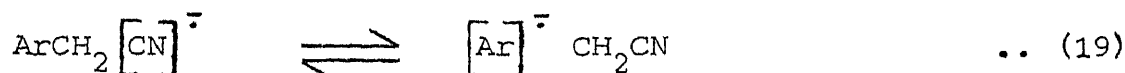


The above reaction scheme explains formation of the disubstituted product, $C_6H_4Y_2$, in preference over the mono-substituted product XC_6H_4Y .

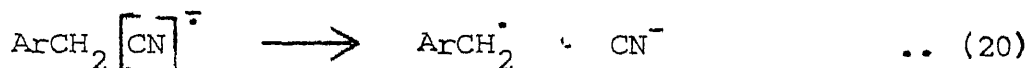
The photostimulated reaction of bromobenzene with cyano-methyl anion is sluggish and yields mainly 1,2-diphenylethane along with a small amount of phenylacetonitrile.¹⁸⁵ The mechanism suggested for this reaction is outlined in Scheme I.23:

SCHEME I.23

Rossi and coworkers^{189,192} have suggested that the intermediate radical-anion formed during the photostimulated reaction of 1-chloronaphthalene with cyanomethyl anion exists as a pair of isomers in equilibrium (Eq. 19):

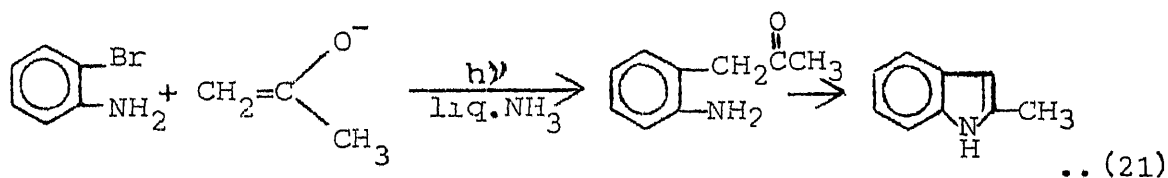


The symbolism of Eq. (19) is meant to indicate that extra-electron resides either in an antibonding (π^*) MO of the cyano group or in the (π^*) MO of the aryl group. MO calculations indicate that the structure $\text{ArCH}_2[\text{CN}]^{\cdot-}$ is more favorable when Ar is phenyl group, but the structure $\text{CNCH}_2[\text{Ar}]^{\cdot-}$ is preferred when Ar is α -naphthyl group.²¹⁵ These authors have proposed that out of the two isomers, only $\text{ArCH}_2[\text{CN}]^{\cdot-}$ undergoes fragmentation according to Eq. (20):



If radical anion $\text{CNCH}_2[\text{Ar}]^{\cdot-}$ is the actual intermediate, then it will be more stable with reference to fragmentation. That is why the reaction of 1-chloronaphthalene with cyanomethylanion yielded α -naphthylacetonitrile. Other ArX compounds¹⁹² in which the lowest unoccupied molecular orbitals of the aryl moieties are at relatively lower energy levels also undergo photostimulated reaction giving substitution product.

Recently, aromatic $\text{S}_{\text{RN}}1$ reactions have been used to synthesize carbocyclic and heterocyclic ring systems. Bard and Bunnett²¹ have, for example, reported the synthesis of indoles from o-haloanilines and acetone enolate anion (Eq. 21):

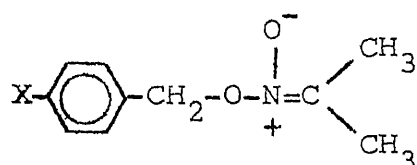


In the same paper, these authors have given experimental proof towards correcting an earlier impression that a dialkylamino-substituent interferes in the aromatic $\text{S}_{\text{RN}}1$ reactions. Following this observation, reports on the synthesis of 2-substituted benzo-[b]-furanes²¹⁷ and 2-azoindoles²¹⁸ via the $\text{S}_{\text{RN}}1$ process have appeared.

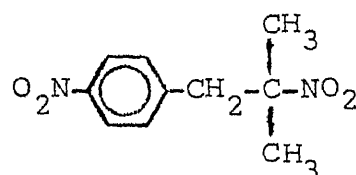
I.6 Aliphatic Substitution by $\text{S}_{\text{RN}}1$ Mechanism

Bender and Hass²¹⁹ observed that while benzylic halides substituted at para-position by groups like CN , $^+\text{NMe}_3$,

COCH_3 , Br or CH_3 , on treatment with 2-nitropropanate anion, give O-alkylation products (XXVIII) and no C-alkylation products, the trend is reversed in the case of para-nitro substituent when C-alkylation product (XXIX) is preferentially formed.



(XXVIII)



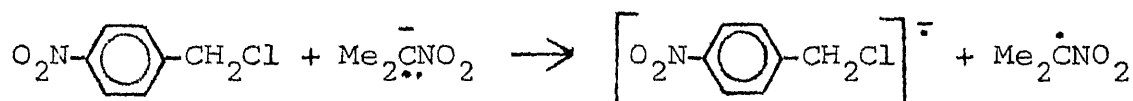
(XXIX)

The O-alkylation can be explained on the basis of $\text{S}_{\text{N}}2$ displacement but the C-alkylation products from ortho- and para-nitrobenzyl chlorides are believed to be derived by a chain process involving radical-anion intermediates.^{178,179}

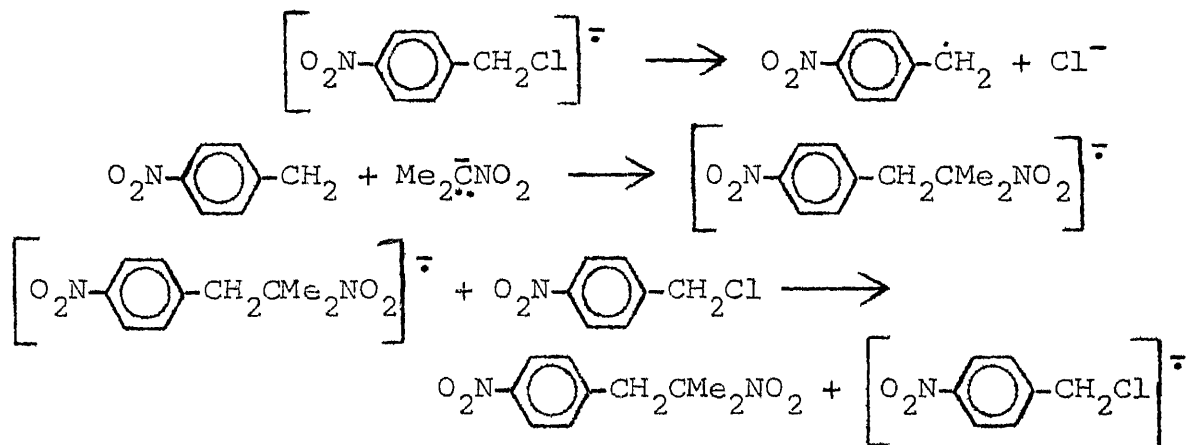
The generalised version of the mechanism for C-alkylation is outlined in Scheme I.24:

SCHEME I.24

Initiation:

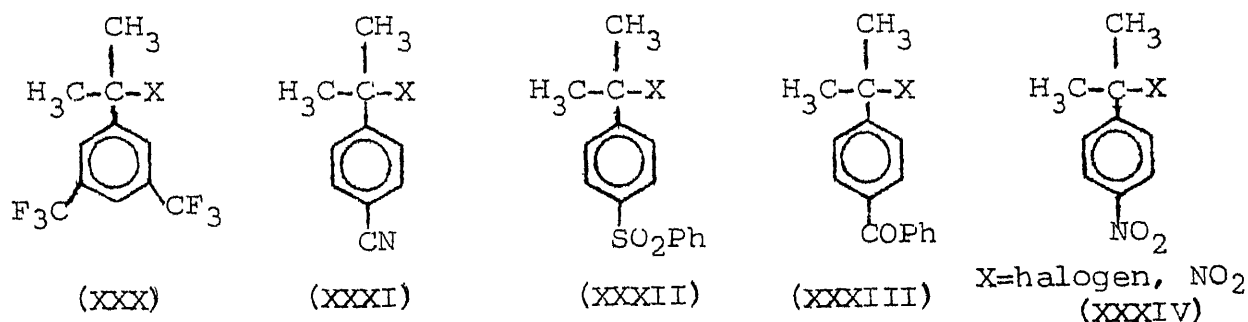


Propagation:

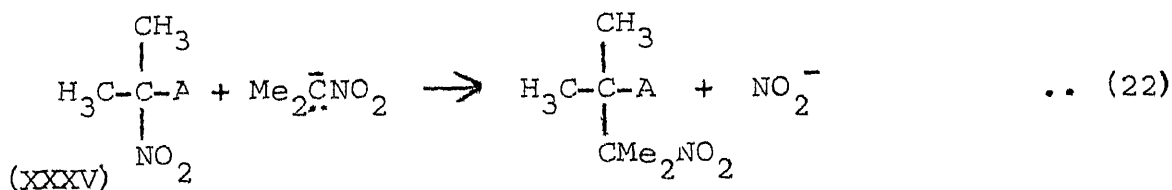


For the corresponding iodides and bromides, the competing S_N2 process leading to O-alkylation^{178b} predominates. The radical chain nature of the above mechanism is established on the basis of the observations that these reactions are inhibited by oxygen²²⁰ and p-dinitrobenzene;²²¹ and accelerated by light.^{220,222} The similarity between the mechanisms of Scheme I.24 and I.20 (aromatic $S_{RN}1$ mechanism) is noteworthy.

The aliphatic $S_{RN}1$ substitution also takes place at tertiary carbon atoms of p-nitrocumyl chloride,²²³ α ,p-dinitrocumene,²²⁴⁻²²⁷ m-nitrocumyl chloride²²⁸ and α ,m-dinitrocumene²²⁸ with numerous nucleophiles. In addition to the p-nitrocumyl system, compounds (XXX) to (XXXIV) have also been reported by Kornblum and coworkers^{22,229,261} to react with 2-nitropropanate anion.

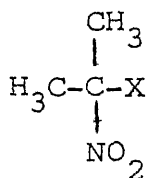


Nucleophilic substitution with 2-nitropropanate anion on purely aliphatic compounds (XXXV) as shown in Eq. (22) has been reported to follow a similar $S_{RN}1$ mechanism.^{227,230,235}



A = COOEt, COPh, CN, NO₂

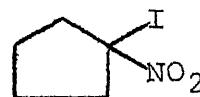
α -Halonitro compounds (XXXVI - XXXVIII), on treatment with nucleophiles, undergo substitution in which the halogen rather than the nitro group is displaced.²³²⁻²³⁶



(XXXVI)




(XXXVII)



(XXXVIII)

X = Cl, Br, I.

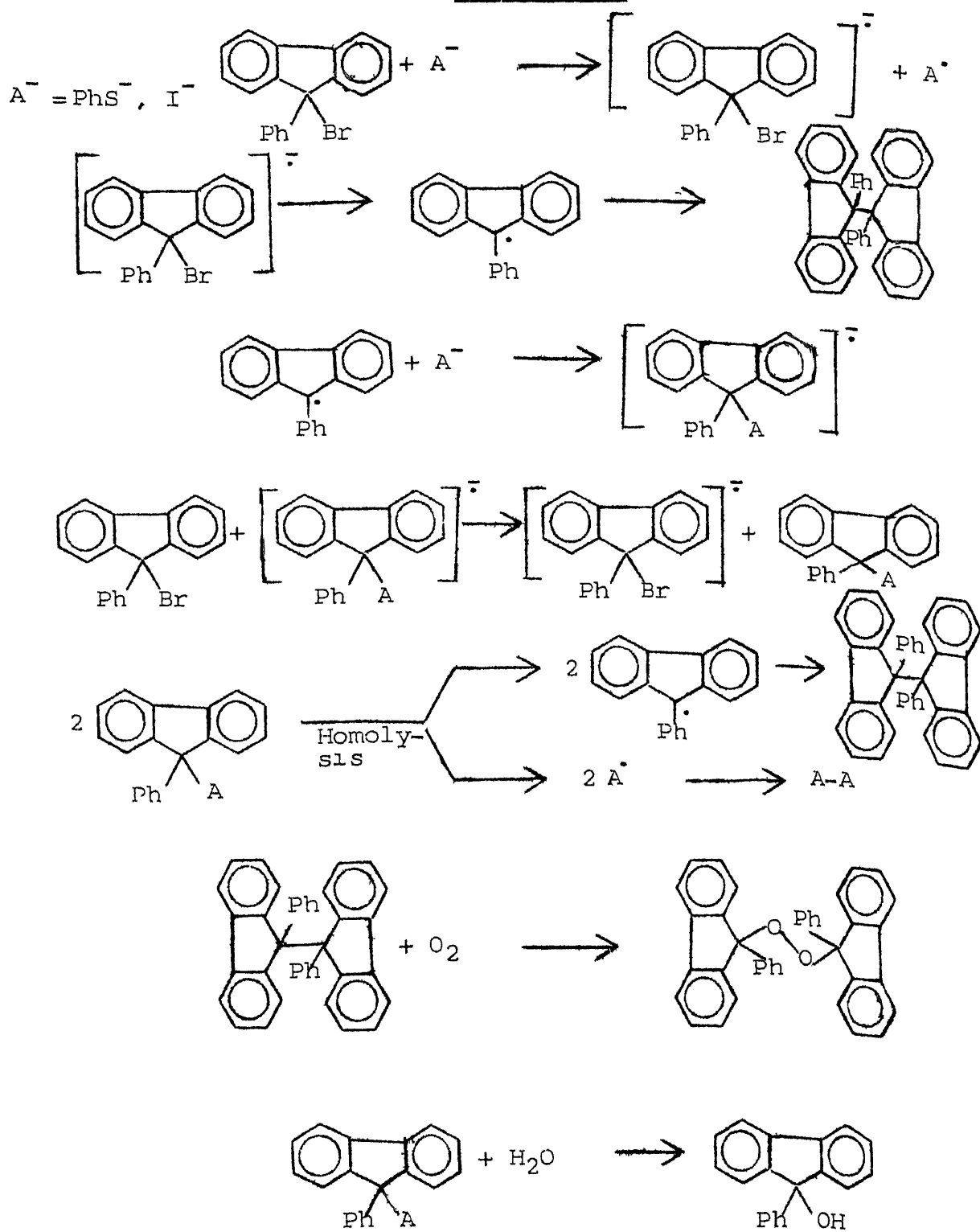
Nucleophiles: $\text{Me}_2\text{C}^-\text{NO}_2$, $\text{EtC}^-(\text{COOEt})_2$, $\text{Me}(\text{CN})\text{C}^-(\text{COOEt})$,

PhSO_2^- ,  NO_2 , alkyl lithiums

Displacement of a sulfone group from α -nitrosulfones has also been reported.²³⁷ It has been found that a cyano group facilitates the electron transfer chain process.²³⁸ α -Nitrosulfides also undergo $\text{S}_{\text{RN}}1$ reaction by nitronate, malonate and sulfinate anions.^{235a} Intramolecular cyclisation using appropriately substituted p-nitrobenzyl chloride²³⁹ has been achieved. All these reactions show the characteristic of a chain process involving radical-anion intermediates.

Singh et al.^{58a} have studied the reactions of 9-bromo-9-phenylfluorene with certain nucleophiles and provided evidences in favor of electron transfer radical-anion mechanism outlined in Scheme I.25:

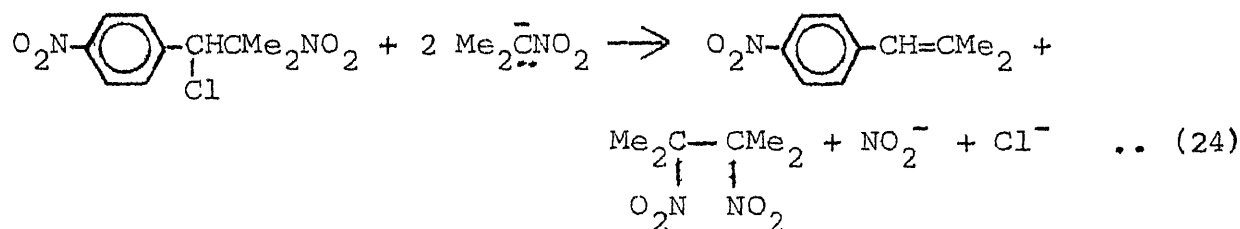
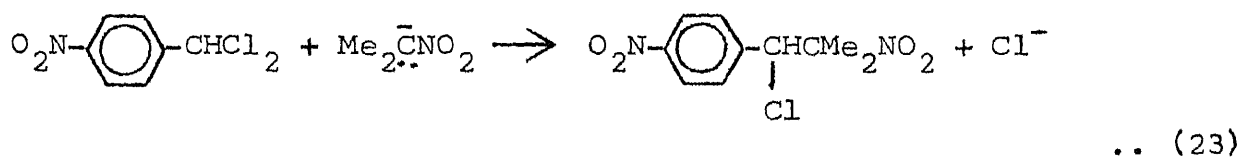
SCHEME I. 25



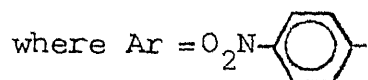
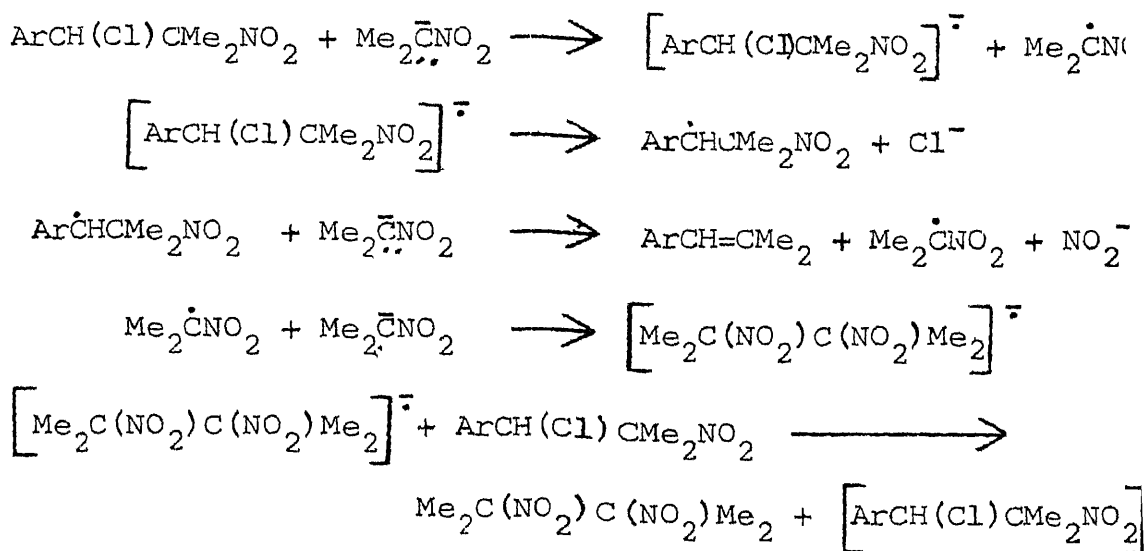
Recently Russell et al. have reported that organomercuric halides react with 2-nitropropanate anion,^{240a} dialkylphosphite anions,^{240b} and sulfinate anions²⁴¹ by $S_{RN}1$ pathway. Reaction of N-(p-nitrobenzyl)pyridinium cation with 2-nitropropanate anion²⁴² has also been reported.

I.7 Elimination Reactions via Electron Transfer

Certain elimination reactions of geminally and vicinally substituted leaving groups are known to occur by electron transfer mechanism. The reaction of p-nitrobenzylidene dichloride with 2-nitropropanate anion is postulated²⁴³⁻²⁴⁵ to be taking place in two steps as shown in Eqs. (23) and (24).

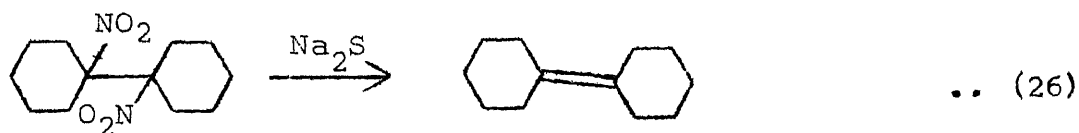
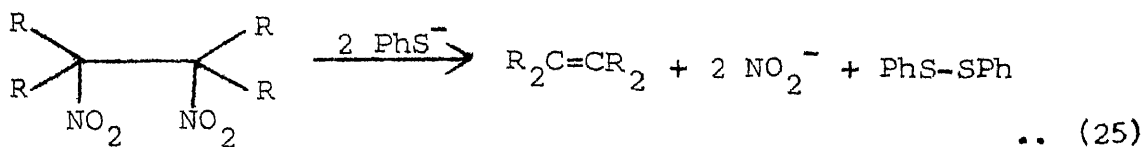


The first process is, undoubtedly, an $S_{RN}1$ reaction.²² The second process has also been shown to be inhibited by p-dinitrobenzene and accelerated by light.²⁴³ Freeman and Norris²⁴³ have proposed the mechanism outlined in Scheme I.26 for the second process postulated in Eq. (24):

SCHEME I. 26

The above pathway has been named²⁴³ as $\text{E}_{\text{RC}}1$ (Elimination, radical Chain, Unimolecular) mechanism.

Kornblum and his coworkers²³⁵ have reported the conversion of vicinal dinitroalkanes into alkenes by treatment with either thiophenoxide or sulfide anions (Eqs. 25 & 26):

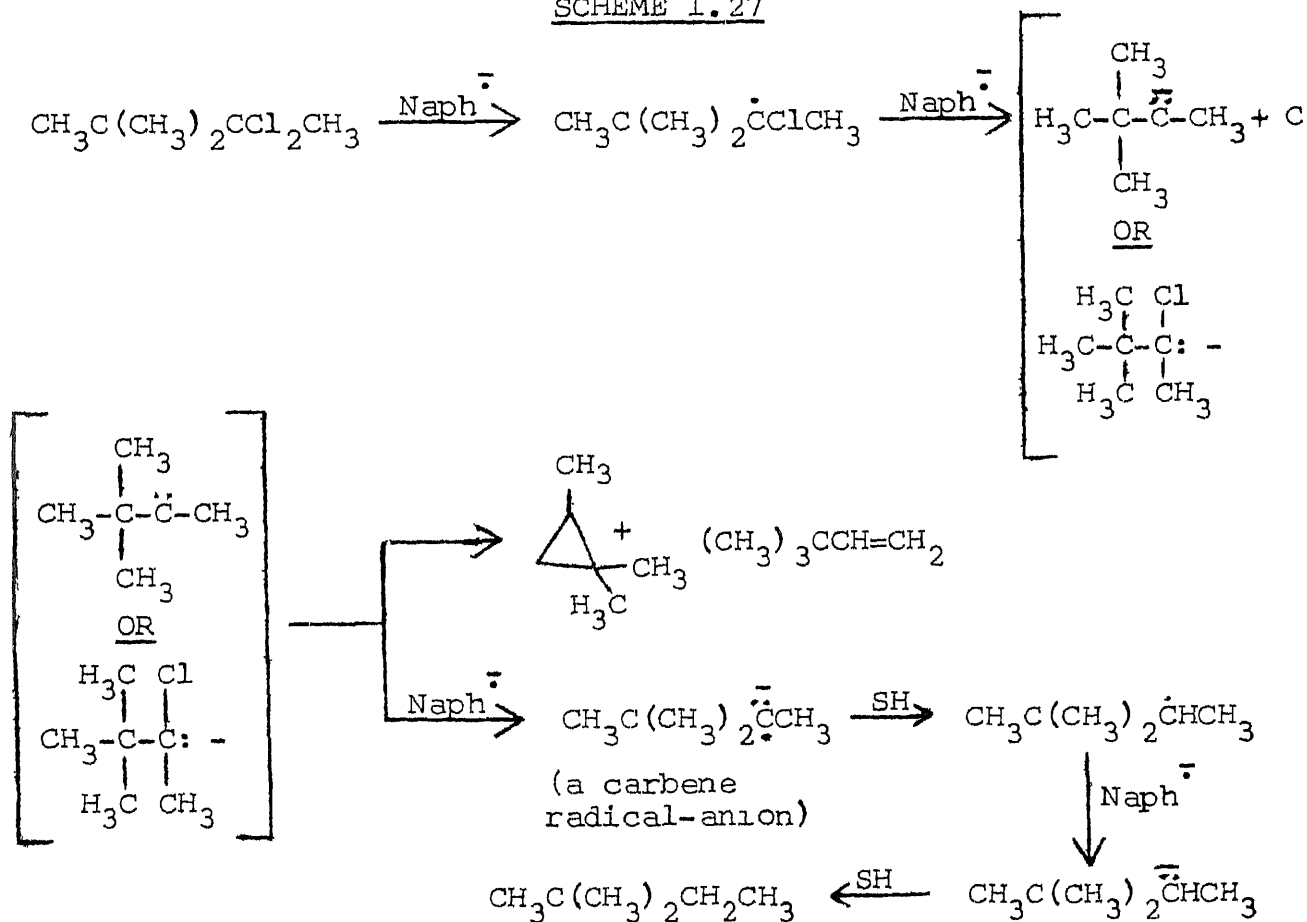


These reactions are believed to occur by $\text{E}_{\text{RC}}1$ mechanism. Vicinal dihalides react readily with sodium naphthalene and disodium

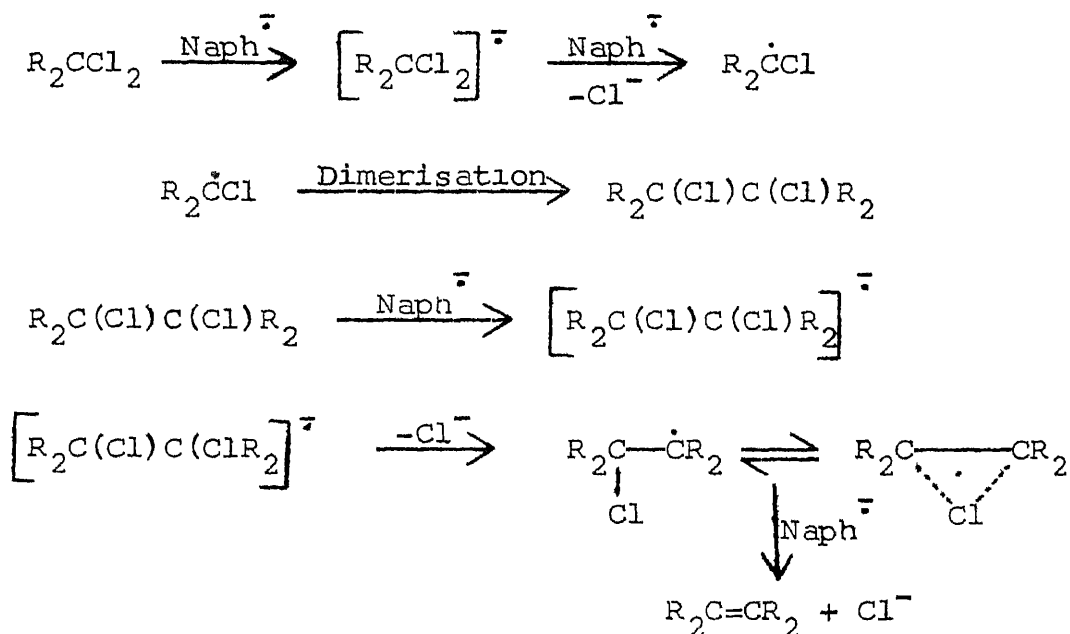
salt of phenanthrene giving olefins.^{246,247}

Sargent and coworkers²⁴⁸ have studied the reaction of a gem-dihalide viz 2,2-dichloro-3,3-dimethylbutane with sodium naphthalene. These authors have proposed the existence of a new reactive intermediate called a carbene radical-anion. The formation of the products of this reaction via "elimination and reduction" pathway are summarised in Scheme I.27:

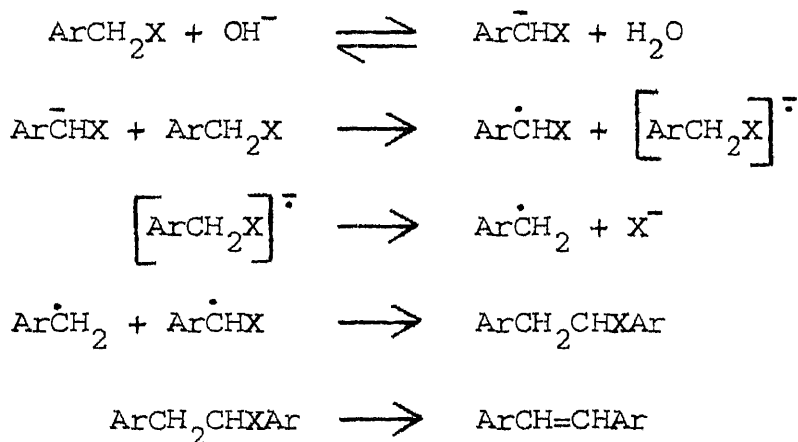
SCHEME I.27



Singh and Jayaraman²⁴⁹ have invoked the presence of bridged radicals in the reaction of gem-dichlorides with sodium naphthalen as shown in Scheme I.28:

SCHEME I.28

Base catalysed elimination reactions of 4-nitrobenzyl-halides and dimethyl-4-nitrobenzylsulfonium ion²⁵⁰ are known. An electron transfer mechanism as outlined in Scheme I.29 has been proposed:²⁵¹

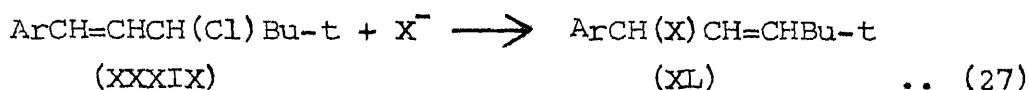
SCHEME I.29

Ar = 4-O₂NC₆H₄; X = Cl, SMe₂

Reductive eliminations of cyclic phosphates,⁴⁰ cyanohydrins,⁴¹ α -nitrosulfones²⁵² and synchronous elimination of the nitro and ester groups or the nitro and keto groups in appropriate substrates have been reported recently.²⁵³

I.8 The S_{RN}1' Reaction

The transformation of (XXXIX) to (XL) shown in Eq. (27) represents the first report of a radical-anion, radical chain substitution reaction with allylic rearrangement. This

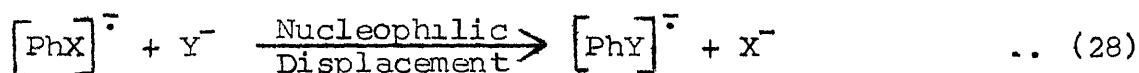


Ar = p-O₂NC₆H₄ and X = Me₂CNO₂⁻ or MeC(COOEt)₂⁻

corresponds to a S_{RN}1' mechanism and has been named so by Norris and Baker.²⁵⁴

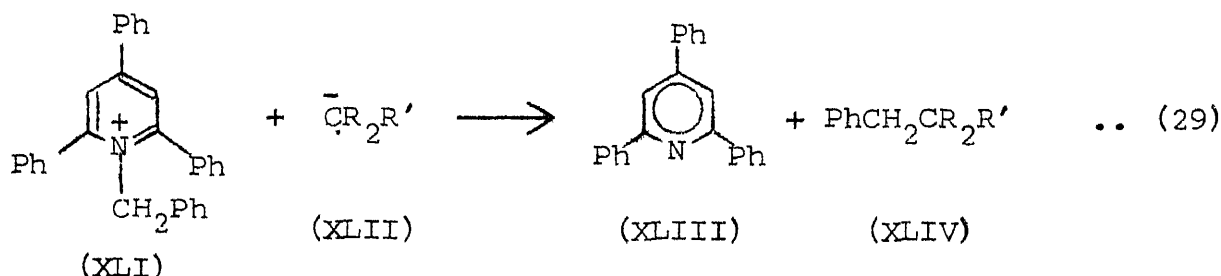
I.9 The S_{RN}2 Mechanism

In this mechanism, the substrate radical-anion [PhX]⁻ undergoes nucleophilic displacement with nucleophile Y⁻, in a single step, to form the product radical-anion [PhY]⁻ (Eq. 28),^{196a} unlike the S_{RN}1 processes which utilise two steps and have the phenyl radicals as intermediates (Scheme I.20).



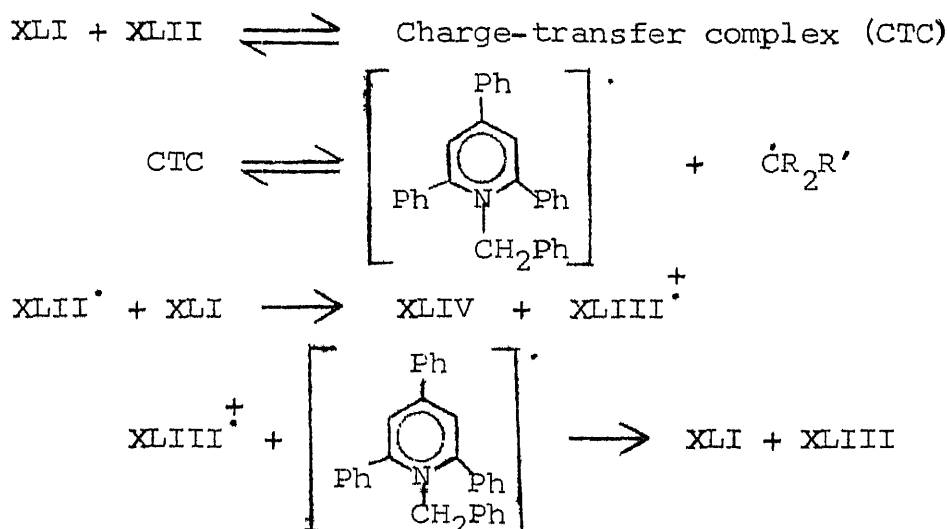
Recently, reactions of 1-alkylpyridinium cations (XLI) with anions derived from nitroalkanes and ethyl malonate²⁵⁵

have been reported (Eq. 29):



These nucleophilic substitution reactions are believed to take place through radicals as shown in Scheme I.31:

SCHEME I.31



This non-chain radical pathway has also been named as $S_{\text{RN}}2$ by Katritzky and coworkers²⁵⁵ in contrast to the one proposed earlier by Bunnett and coworkers.^{196a}

It is evident from the above description that many reactions known to proceed by uncertain pathways present challenging opportunities for mechanistic investigations. We, therefore, decided to study a few reactions described in the following chapters which initially appeared to involve free radical intermediates and now found by us to involve electron transfer processes.

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and AlHX_3^- when formed in the reaction medium serve the same purpose as inferior alternatives to AlH_4^- with efficiency decreasing in the order: $\text{AlH}_3\text{X}^- > \text{AlH}_2\text{X}_2^- > \text{AlHX}_3^-$.

Reductive cyclization of Z-2-chlorostilbene also involves electron transfer from AlH_4^- producing aryl radicals. These radicals preferentially cyclize to give phenanthrene in good yields but also pick up a hydrogen atom from AlH_4^- giving Z-stilbene. LAH-induced isomerization of Z-stilbene to E-stilbene supports the view on electron donating capability of LAH.

II.2 Introduction

LAH has been known for over thirty years as one of the most versatile reducing agents in organic chemistry. Since its discovery¹ in 1947, the uses of this reagent have become a legend. Inability of the catalytic hydrogenation method to selectively reduce carbonyl functions of ketones, acids, esters and amides in the presence of carbon-carbon multiple bonds led to the growing interest in complex metal hydride reductions² which serve the purpose. Its violent reaction with water resulting in the liberation of hydrogen and decomposition of the reagent by protic solvents do not permit use of LAH for the reduction of substances which dissolve only in water or other protic solvents. However, substances soluble in ethereal solvents such as diethyl ether and tetrahydrofuran are reduced by LAH readily and in some cases, quantitatively. Though many

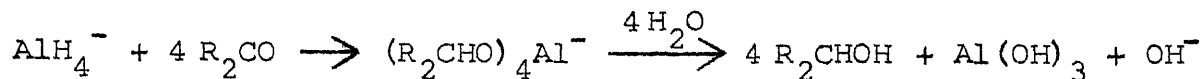
complex metal hydrides have been developed, but more attention has been preferentially focussed on LAH, sodium borohydride (SBH), tri-n-butyltinhydride ($n\text{-Bu}_3\text{SnH}$) and diborane (B_2H_6). The scope and limitations of the reducing action of complex metal hydrides have been reviewed extensively.³⁻⁹

Table II.1 shows some typical functional groups well known to undergo reduction with LAH.

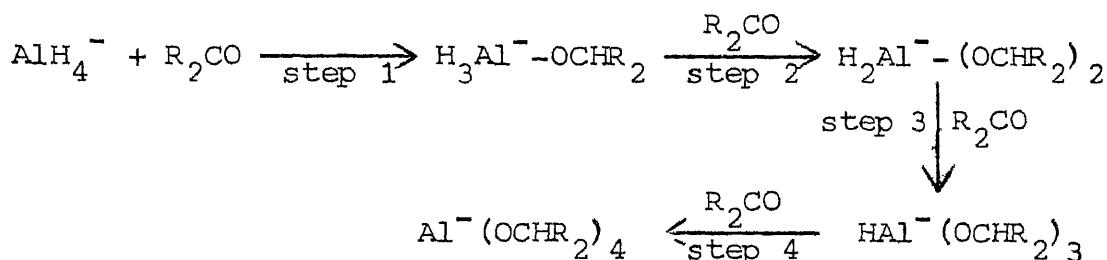
Table II.1 Common Functional Groups Reduced with LAH

Functional group(s)	Major product(s)
>C=O	>CHOH
$-\text{CO}_2\text{R}$	$-\text{CH}_2\text{OH} + \text{ROH}$
$-\text{COOH}$	$-\text{CH}_2\text{OH}$
$-\text{CONHR}$	$-\text{CH}_2\text{NHR}$
$-\text{CONR}_2$	$-\text{CH}_2\text{NR}_2$ or $-\text{CHO} + \text{R}_2\text{NH}$
$-\text{C}\equiv\text{N}$	$-\text{CH}_2\text{NH}_2$
>C=NOH	>CHNH_2
>C-NO_2	>C-NH_2
Ar-NO_2	Ar-N=N-Ar
$-\text{CH}_2\text{X}$ (X = halogen, OTs, OBs or any such good leaving group)	$-\text{CH}_3$
>CH-X (X = halogen, OTs, OBs, etc.)	>CH_2
-CH-C- O O	$-\text{CH}_2-\text{C-}$ OH

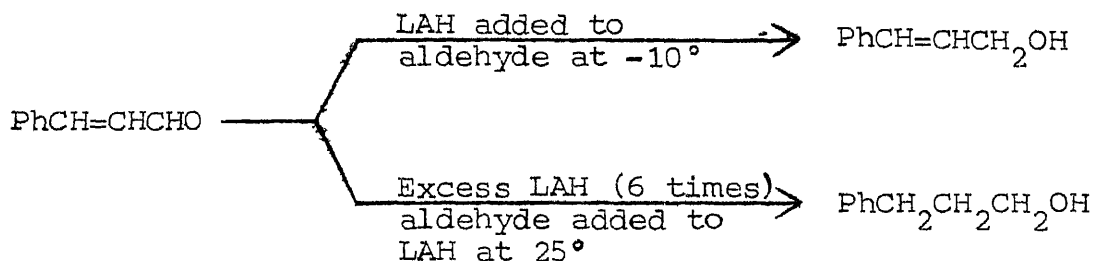
The reduction of an aldehyde or a ketone with LAH is thought to involve the transfer of a hydride ion to the carbonyl function:



Since all the four hydrogen atoms of LAH can be used for reduction, the occurrence of a series of consecutive reactions¹⁰ shown below is apparent:

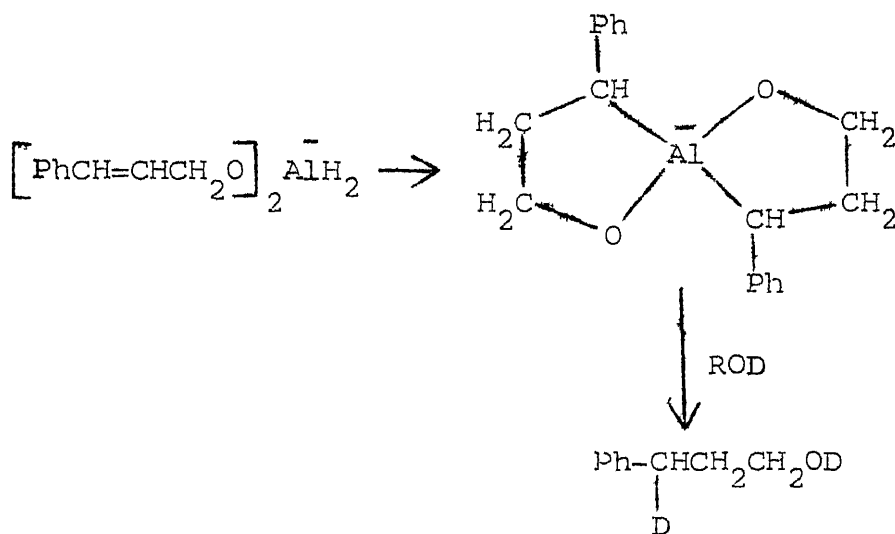


After the first step, it is observed that every subsequent step is slower than the step immediately preceding it: i.e., step 1 > step 2 > step 3 > step 4. Unlike isolated carbon-carbon double bonds, activated double bonds have been reduced with LAH^{11,12} as shown below:

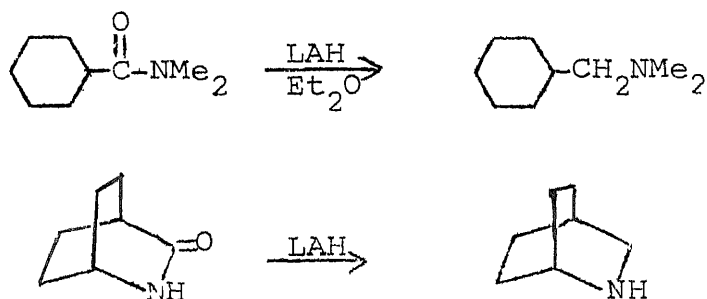


These reductions are believed to involve an organoaluminium

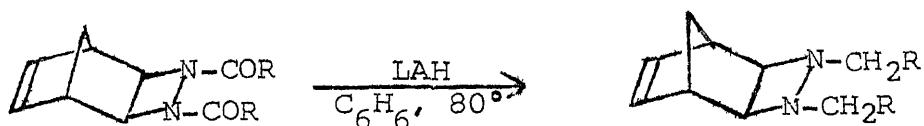
complex as intermediate:



Reduction of carbonyl groups attached to a nitrogen function has also been reported:^{13,14}

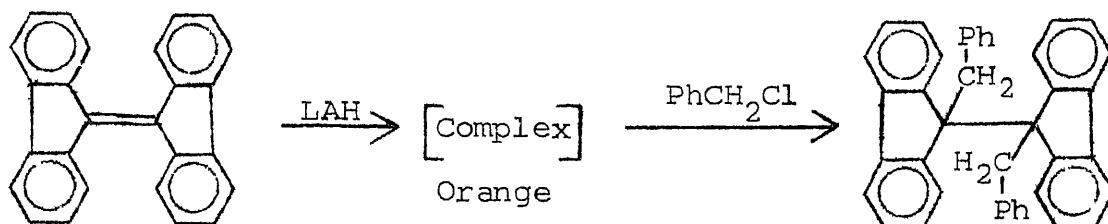


Reduction of 1,2-diaroyl-1,2-diazetidines with LAH¹⁵ at 80° results in the transformation of both carbonyl groups into methylene groups:



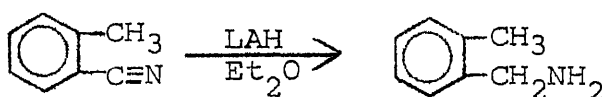
when $R = C_6H_5$, $p\text{-MeOC}_6H_4$ and $p\text{-CF}_3C_6H_4$; whereas reduction at 22° yields exclusively monoaroyl-1,2-diazetidine when R is a phenyl group.

Normal double bonds in bifuorenylidene and similar strained fulvenes are known to undergo reduction with LAH.¹⁶

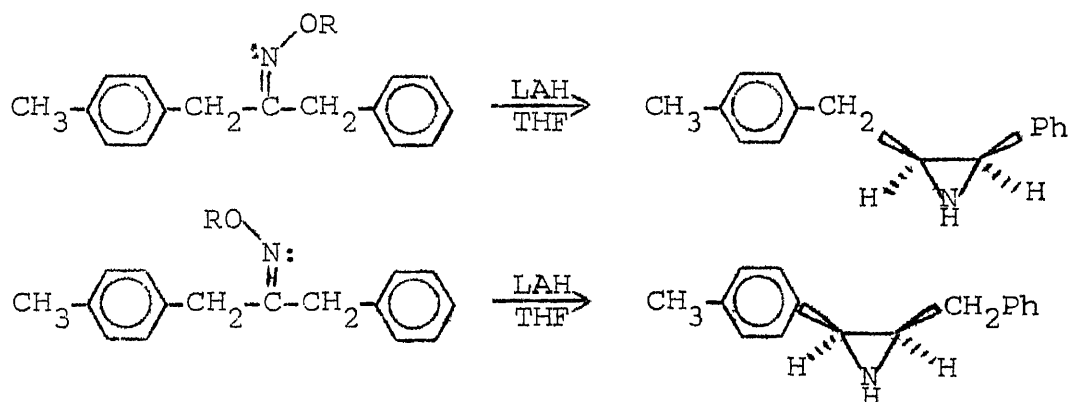


The reduction of substituted diarylolefins has also been achieved.¹⁷

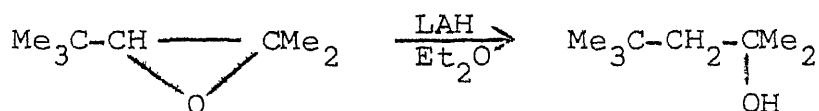
Nitriles are reduced to the corresponding amines:¹⁸



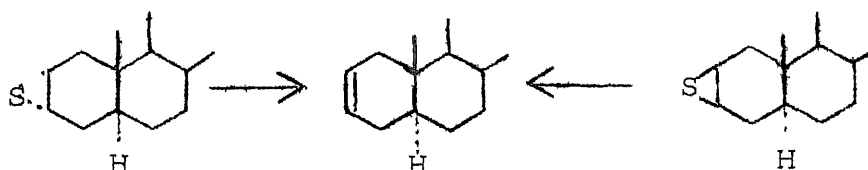
The LAH reduction of oximes yields primary amines. Aziridines are produced from the reduction of benzylic ketoximes^{21,22} with LAH. The reactions proceed with a high degree of stereospecificity:



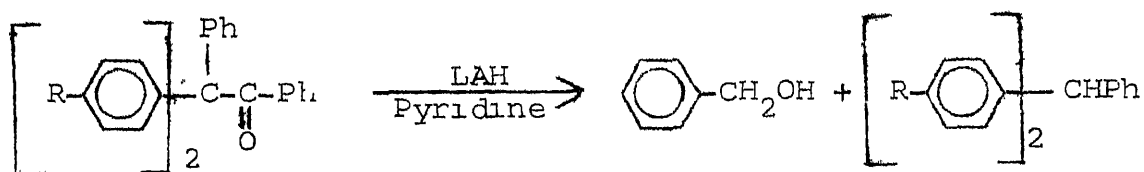
Epoxides have been reported to undergo reduction via a S_N2 attack by H^- ion in free or bound state at less hindered position giving more highly substituted alcohol.^{23,24} Exceptions to this generalization have also been reported in the literature.²⁵



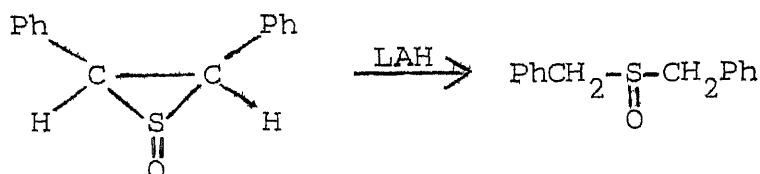
The reduction of episulfides with LAH results in olefin formation:^{26,27}



Scission of C-C bond has been observed in the reduction of benzpinacolones²⁸⁻³² with LAH:

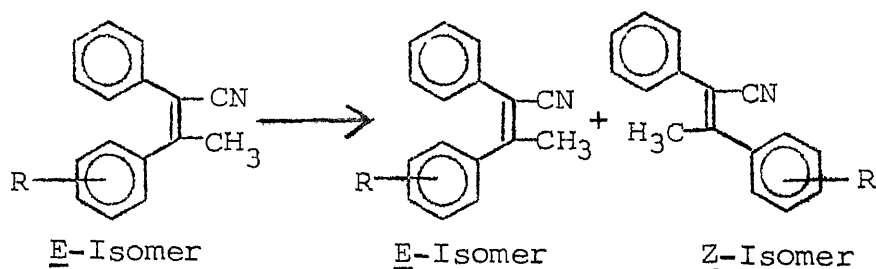


The C-C bond cleavage has also been observed during LAH reduction of a terminal propargyl alcohol³³ and episulfones.³⁴

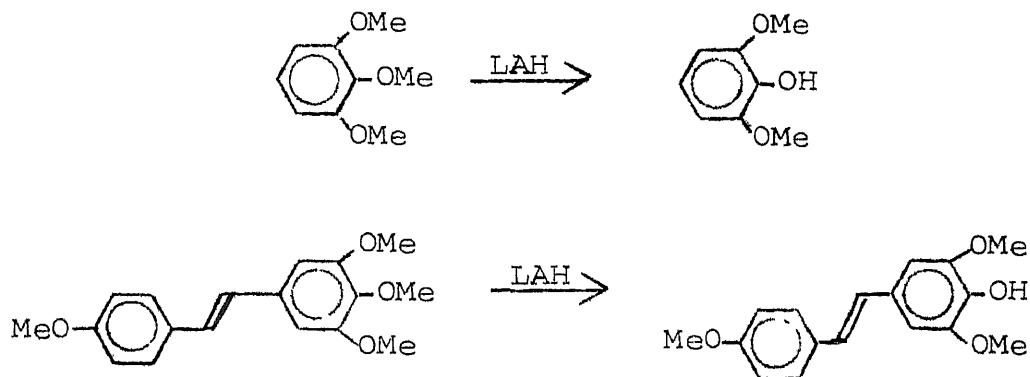


Isomerisation of E-isomers of α -phenyl- β -methylcinnamionitrile and α -phenyl- β -methylchlorocinnamionitrile has been

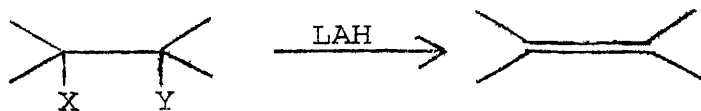
achieved during LAH reductions:³⁵



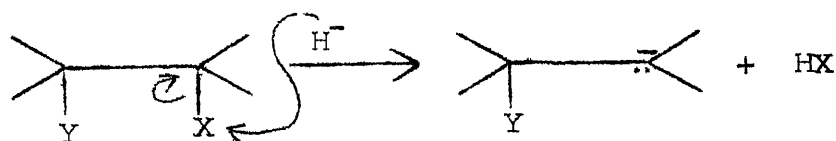
Ethers are generally resistant to attack by LAH; but a few reactions of ether cleavage have been reported in the literature. For example, methyl phenyl ethers undergo selective demethylation with LAH³⁶ in benzene or heptane.

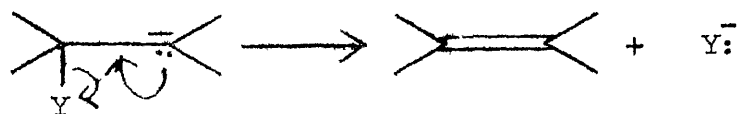


King and Pews³⁷ have reported a few interesting examples of reductive eliminations of 1,2-dihalides and 1,2-dibromohydrin-p-toluenesulfonates:

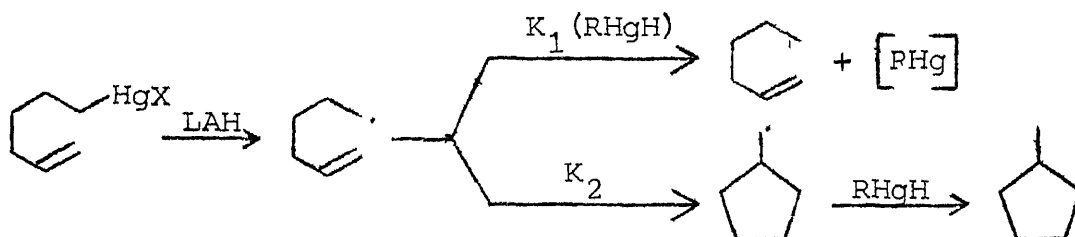


These reductions are visualized to occur by the path outlined below:

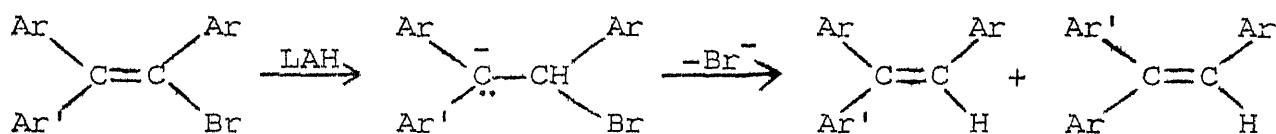




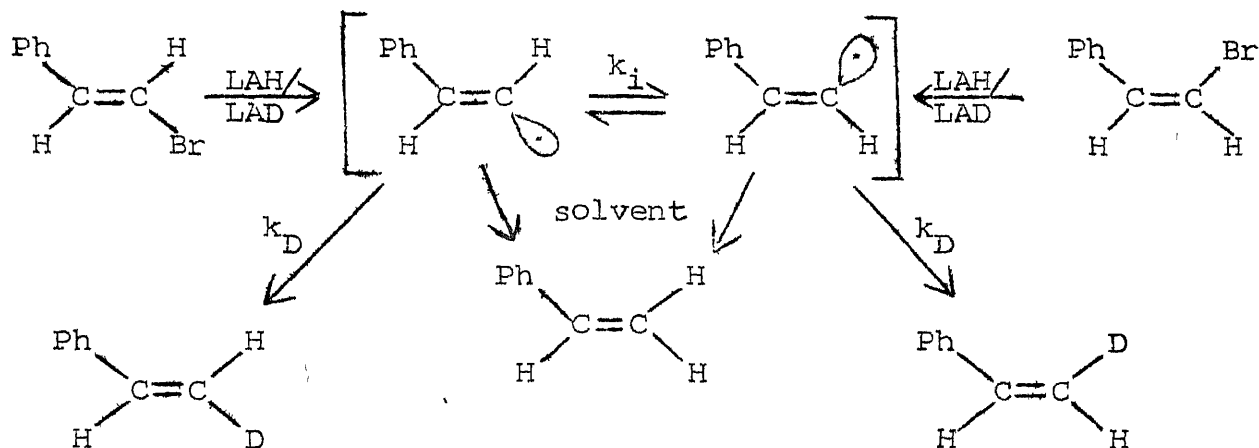
Free radical intermediates have been proposed recently in the reactions of alkylmercuric halides with LAH:³⁸



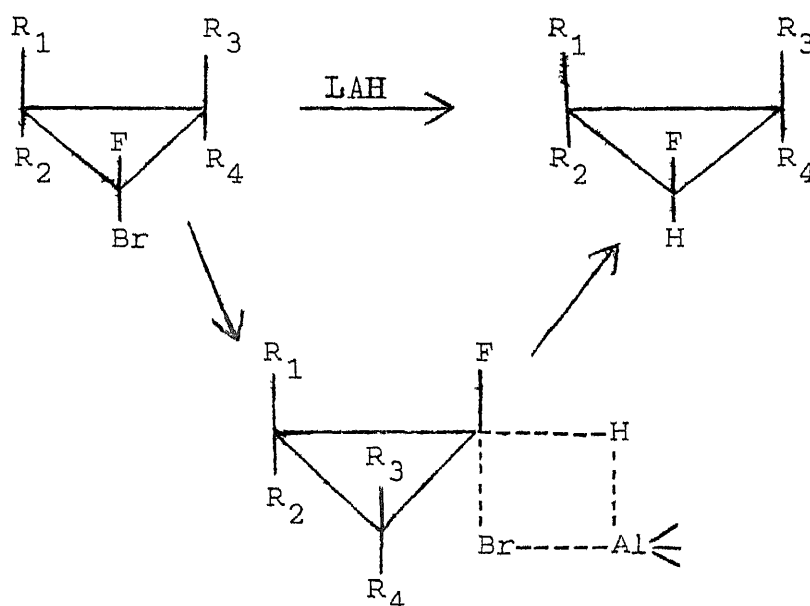
Reduction of triphenyl vinyl bromides with LAH yields the corresponding styrenes.³⁹ cis-Vinyl halides yield a 1:1 mixture of cis- and trans-styrenes. An addition-elimination mechanism outlined below has been proposed:



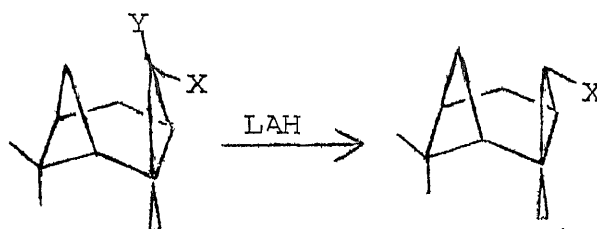
Recently, the involvement of free radicals has been suggested in the reduction of cis- and trans- β -bromostyrenes⁴⁰ with LAH and LAD, as shown below:



Reduction of gem-bromofluorocyclopropanes with LAH in tetrahydrofuran proceeds stereospecifically with retention of configuration,⁴¹ presumably via a four centred transition state shown below:



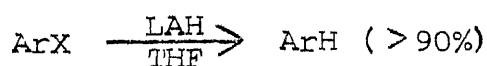
LAH reductions of some other gem-dihalides shown below are believed to involve free radical intermediates:⁴²



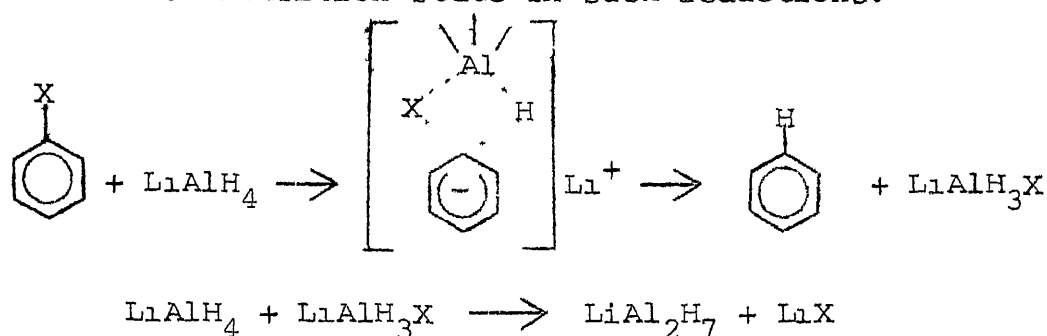
a) $X=Y=Cl$; b) $X=Y=Br$;
c) $X=Cl$, $Y=Br$.

a) $X=Cl$; b) $X=Br$; c) $X=Cl$.

Aromatic halides have also been reduced by LAH in refluxing THF.⁴³⁻⁴⁵ Bromobenzene and iodobenzene react rapidly giving high yields of the dehalogenated product.⁴⁶

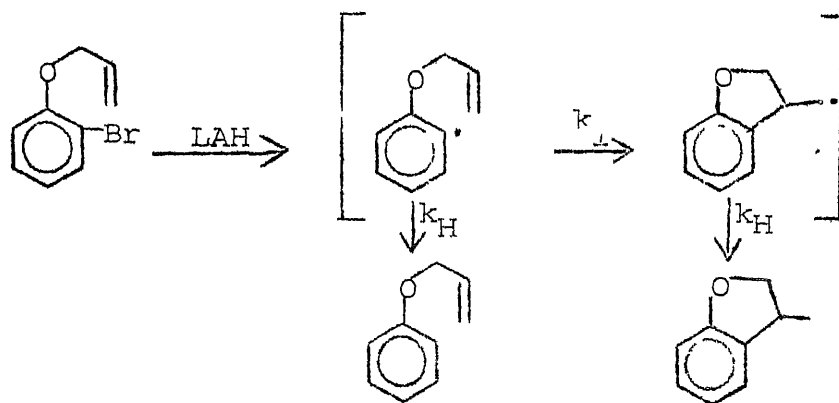


Brown and Krishnamurty⁴⁷ have suggested the intervention of a four-centred transition state in such reductions:



The order of reactivities of, halogens in such reductions is $\text{I} > \text{Br} > \text{Cl} > \text{F}$ which also happens to be the order of reactivities of halides involving free radical intermediates.⁴⁸

Reduction of o-bromophenyl allyl ether with LAH yields phenyl allyl ether and 3-methyl-2,3-dihydrobenzofuran. A mechanism involving free radical intermediates has been proposed:⁴⁹

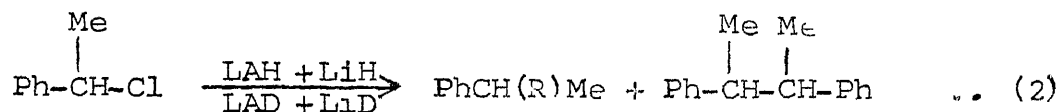
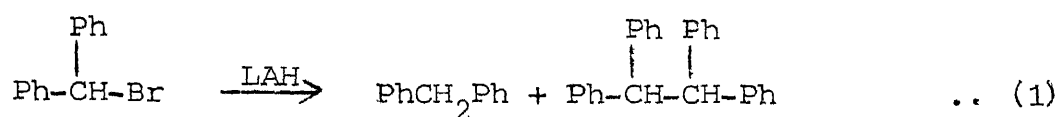


Recently, single electron transfer in the LAH reductions of ketones and alcohols has also been reported.⁵⁰

In view of the mechanistic uncertainties in the reactions of LAH with various substrates especially the organic halides, we undertook a study of the reactions of LAH with benzylic halides and Z-2-chlorostilbene in detail so as to ascertain the reaction pathway.

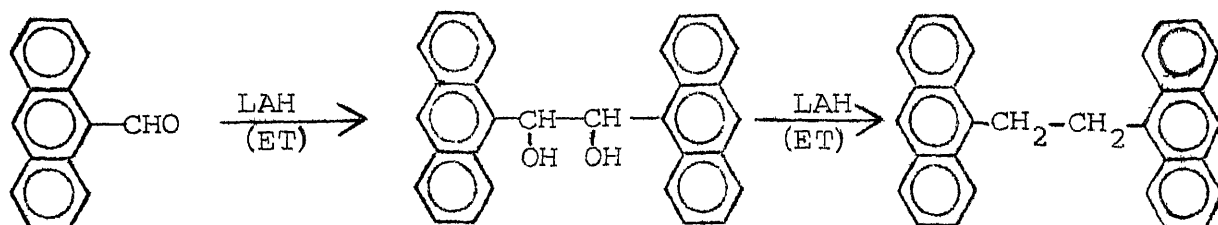
II.3 Results and Discussion

LAH is traditionally thought to involve a nucleophilic attack by the hydride ion in bonded or free state. However, in some of the reactions involving LAH, nucleophilic attack by the hydride ion is not so obvious as usually thought.⁵¹ The reduction of 9-formylanthracene to give 1,2-di-(9-anthryl)-ethane⁵¹ or formation of tetraphenylethane⁵² in reaction (1) and that of 2,3-diphenylbutane⁵³ in reaction (2) are such examples:



R = H, D.

Whereas the LAH reduction of 9-formylanthracene to 1,2-di-(9-anthryl)-ethane can be now rationalized in terms of an electron transfer process (not a nucleophilic process !) similar to that reported⁵⁰ recently,



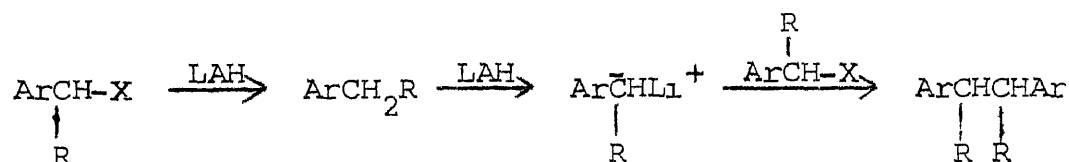
we note here that the occurrence of reactions (1) and (2) cannot be rationalized on the basis of a nucleophilic attack by H⁻ ion

unless the unlikely approach of H^- to the partially negatively charged halogen is assumed.

We undertook the present study with a view to establishing the mechanisms of LAH reductions with reference to a few selected substrates. The occurrence of a radical component in a few reactions has been conclusively proved by us using chemical and ESR studies. Reductions of 9-chloromethylantracene Ia, diphenylchloromethane Ib and 9-bromofluorene Ic were carried out in dry THF at ice-bath temperature under inert atmosphere by the addition of LAH contained in tetrahydrofuran. Different molar ratios of the halide to LAH were used during these reductions. Characteristic transient green, yellow and red colors developed, respectively which deepened in the beginning but slowly faded away as the reaction proceeded forward. Evolution of hydrogen gas was observed in all the reactions. The product distribution of these reactions is listed in Table II.2.

The suggestion of Trevoy and Brown⁵² that the dimeric product might be arising from the metallation of initially formed reduction product $-ArCH_2R$, followed by a nucleophilic attack of the carbanion on the organic halide (Scheme II.1)

SCHEME II.1



has been ruled out on the basis of our inability to get any

Table II.2. Reaction^a of I, Ar-CH(R)-X (0.01 mol) with LAH in dry THF at ice-bath temperature under inert atmosphere

Halide	Run	LAH mol	Reaction time, min.	% Products			
				$\left[\text{Ar-CH(R)}\right]_2$	Ar-CH ₂ -R	Starting halide	H ₂ ^b
Ia	1	0.01	35	64	23	-	63
Ia	2	0.005	35	42	16	32	70
Ia	3	0.0025	35	35	11	44	75
Ia	4	0.0025	240	40	13	36	82
Ib	5	0.01	35	42	25	-	58
Ib	6	0.005	35	36	13	27	63
Ib	7	0.0025	35	26	9	37	72
Ib	8	0.0025	240	31	10	30	75
Ic	9	0.01	35	72	20	-	58
Ic	10	0.005	35	51	14	30	80
Ic	11	0.0025	35	42	8	40	100
Ic	12	0.0025	240	46	10	34	100

a, On mixing the reactants green, yellow and red colors developed immediately in the cases of Ia, Ib and Ic respectively; Ib also yielded fluorene 7%, 5% and <5% in runs 5, 6, 7 and 8 respectively.

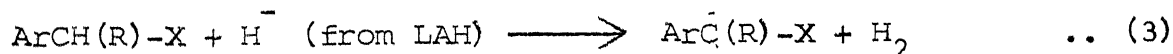
b, Volume of H₂ determined at atmospheric pressure by comparison with control experiments in the absence of I using same batch of reactants and solvent under identical conditions and percentage calculated based on the availability of only one out of four hydrogens of LAH.

deuterium incorporated product in the reactions of LAH with fluorene, diphenylmethane and 9-methylanthracene under the original conditions and subsequent work up in the presence of D_2O .

We consider the approach of a hydride ion to the negative halogen end of the C-X: dipole in $ArCH(R)-X$ as improbable. This view makes the formation of a carbanion via abstraction of a halonium ion followed by subsequent attack on the halide to yield dimer unlikely:



The possibility of abstraction of a proton by hydride ion (Eq. 3) leading to the formation of α -halocarbanion with simultaneous

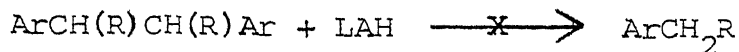


evolution of hydrogen gas is ruled out on the basis of total absence of deuterium in the unreacted starting halides recovered in runs 1, 5 and 9 on quenching each reaction with D_2O after 5 minutes.

The possibility of formation of dimers by the reduction of corresponding compounds of the type - $ArC(R)=C(R)Ar$ - thought to arise via heterolytic reaction of the halide with LAH received our attention; but in control experiments with



tetraphenylethylene and 9,9'-bifluorenylidene under otherwise similar conditions, no reduction was observed. Similarly, conceivable cleavage of the central C-C bond in dimers giving corresponding monomeric products- ArCH_2R - is ruled out on the basis of control experiments with authentic samples of



1,2-di-(9-anthryl)ethane, tetraphenylethane and 9,9'-bifluorenyl wherein the starting hydrocarbons were recovered unchanged.

The intermediacy of radicals in these reactions was proved by the strong ESR signals observed in the reactions of LAH with benzhydryl chloride and 9-bromofluorene which were not present in the pure reactants. The intensity of these signals was found to increase in the beginning but started decreasing after some time. A multiple line ESR signal was observed when p-nitrobenzyl bromide was mixed with LAH. The signal was found to be fairly long-lived as expected due to electron withdrawing effect of the nitro group.

In view of the foregoing observations, we conclude that the reactions under consideration are triggered off by fast transfer of an electron from either AlH_4^- or the hydride anion (made available from the dissociation $\text{AlH}_4^- \rightleftharpoons \text{AlH}_3 + \text{H}^-$) to the low lying vacant antibonding molecular orbital of the organic halide producing radical-anion of the organic halide, hydrogen gas and aluminium hydride simultaneously, as shown in step (i) of Scheme II.2.

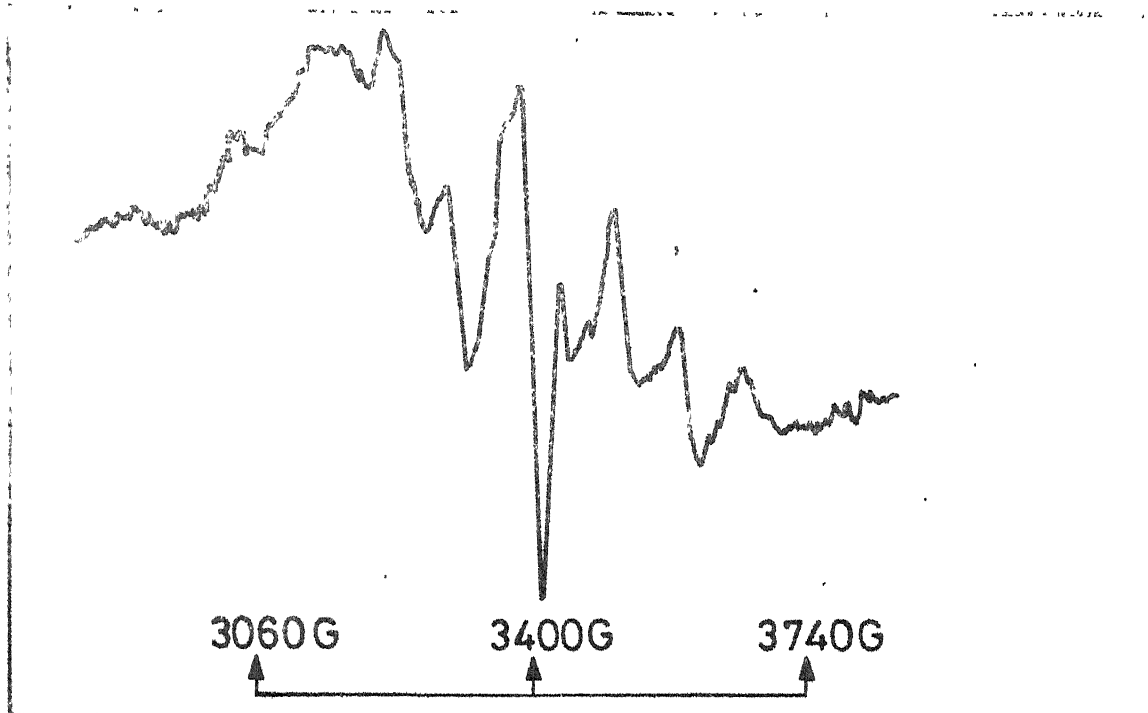


Fig. II.1 ESR spectrum recorded during the reaction of benzhydryl chloride with LiAlH_4 .

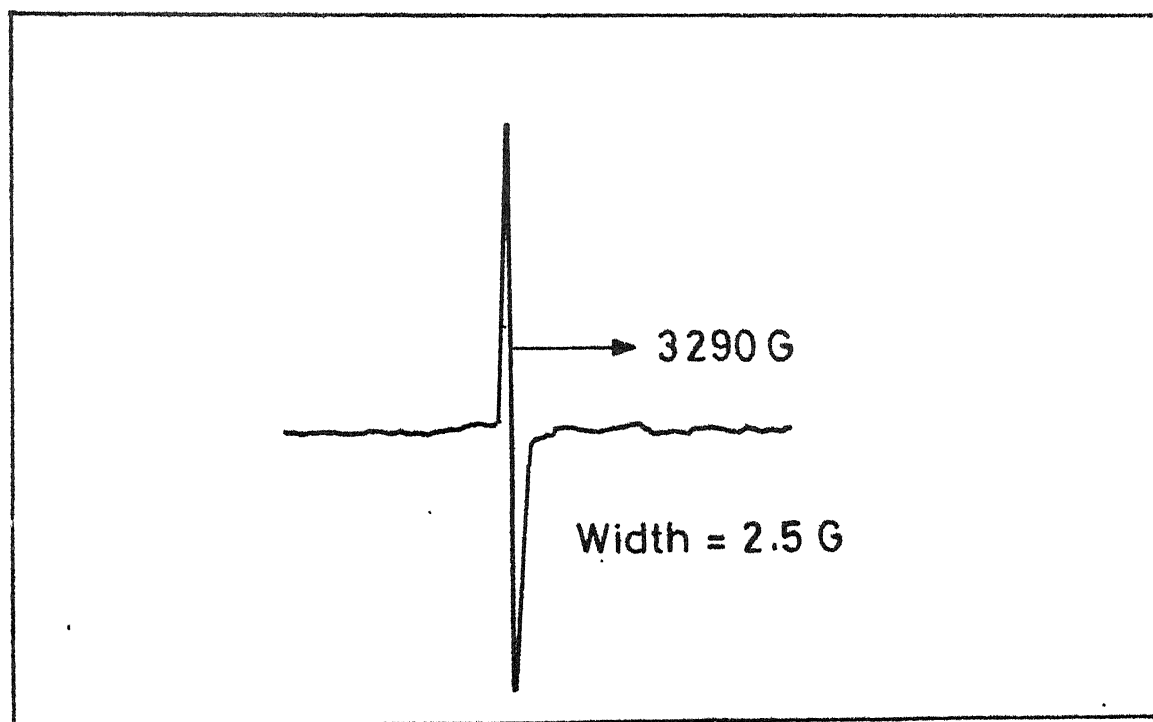
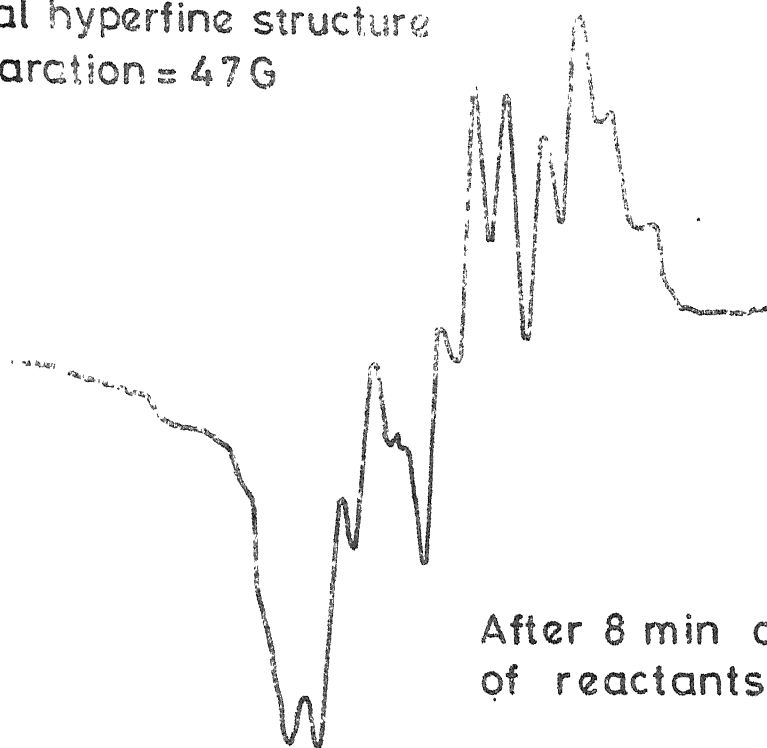


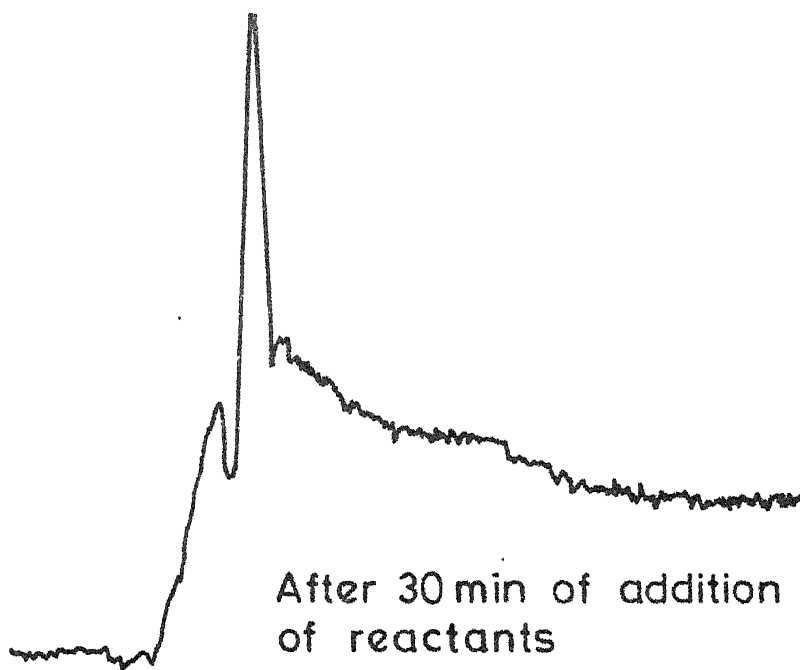
Fig. II.2 ESR spectrum recorded during the reaction of 9-bromofluorene with LiAlH_4 .

Total hyperfine structure
separation = 47 G



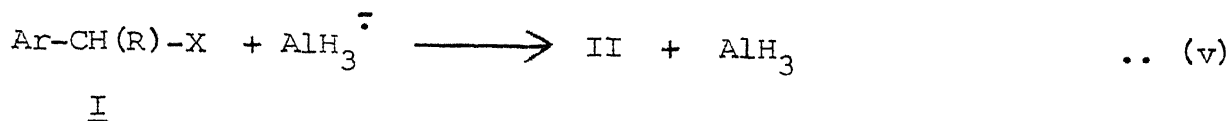
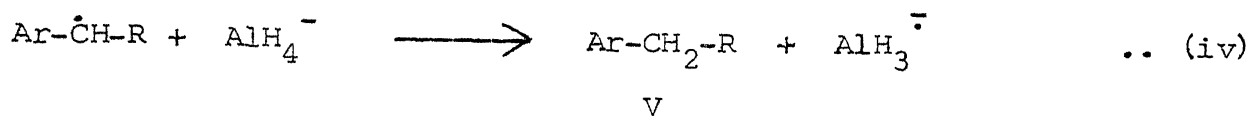
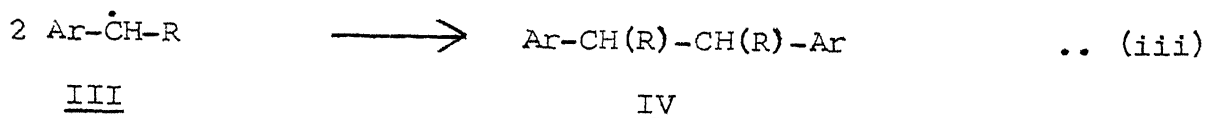
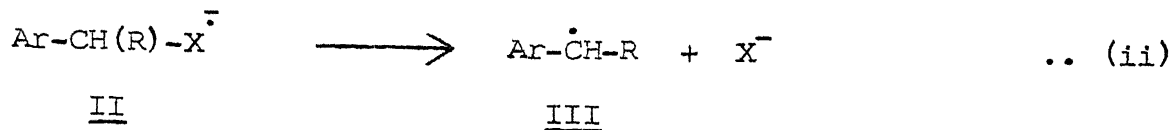
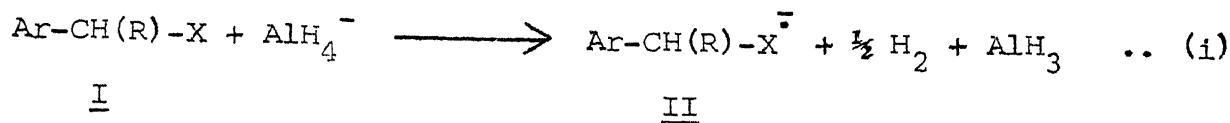
After 8 min of addition
of reactants.

17 G



After 30 min of addition
of reactants

Fig.II.3 ESR spectrum taken at different times during
the reaction of p-nitrobenzyl bromide with LAH.

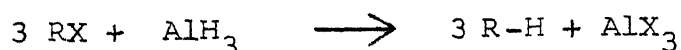
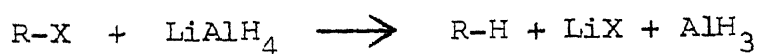
SCHEME II.2

The radical-anion II, once formed, dissociates to give free radicals III (step ii). The benzylic radicals III are known to prefer dimerisation via step (iii) rather than hydrogen abstraction from THF solvent.⁵⁴ A look at the quantity of hydrogen gas evolved in accordance with step (i) on one hand and the formation of substantial amounts of V on the other, makes the existence of hydrogen atom abstracting process represented by step (iv) obvious. Abstraction of a hydrogen atom by radical species from AlH_4^- is precedented.^{40,49,50} Besides producing monomeric reduction product V, step (iv) generates the radical-anion, AlH_3^\cdot which competes with AlH_4^- in donating an electron to the halide. Combination of steps (i to v) accounts for the

11

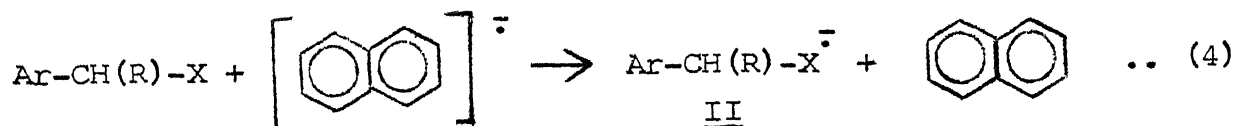
involvement of only one out of four hydrogens available in AlH_4^- in the reduction process. But the consumption of significantly more than 50% of I in runs 2, 6 and 10 where only half the molar quantity of LAH was used and similarly, significantly more than 25% of I in runs 3, 7 and 11 with only one-fourth molar quantity of the reducing agent indicate utilisation of the remaining hydrogens of AlH_3 in these cases.

Johnson, Blizzard and Carhart⁴³ have proposed the overall reduction of four moles of halide with one mole of LAH as taking place in two steps:

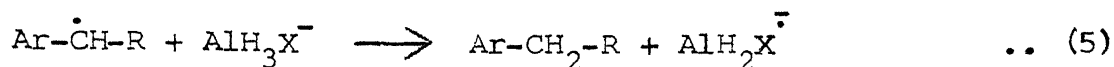


An investigation of this process using equimolar quantity of AlH_3 , prepared in situ,⁵⁵ with 9-bromofluorene under otherwise unchanged reaction conditions showed that no reaction had occurred thus disproving the above hypothesis. On repeating the above reaction by replacing one-fourth of AlH_3 with equal number of moles of sodium naphthalene,⁵⁶ bifluorenyl (40%), fluorene (11%) and starting halide (40%) were obtained.

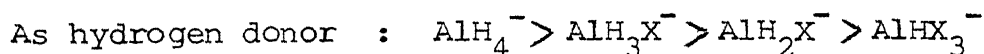
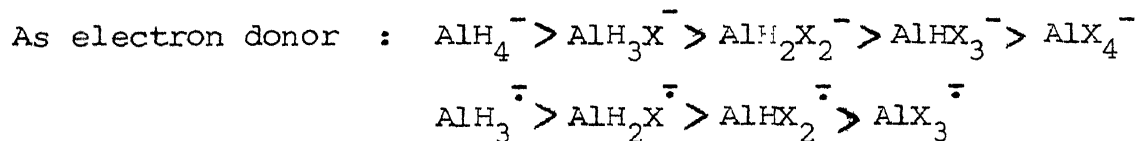
These results are consistent with the well known ability of sodium naphthalene to act as electron donor.⁵⁶ Equation 4, therefore, represents the initiating process in place of step (i):



The halide ion, X^- produced from II (step ii) combines⁴⁷ with AlH_3 present in the medium giving AlH_3X^- . The latter anion can act as a source of hydrogen atoms (Eq. 5):



Species AlH_3X^- and $AlH_2\dot{X}^-$ can also donate electrons as inferior alternatives to AlH_4^- and $AlH_3\dot{-}$, respectively. It is logical that species of the type $AlH_2X_2^-$, $AlHX_3^-$ and AlX_4^- may also be similarly formed in the medium in succession. The first two of these would, to some extent, act as hydrogen atom donors producing radical-anions, $AlH_2\dot{X}^-$ and $AlX_3\dot{-}$, respectively. The expected order of efficiency in reactivities of alanates and alane radical-anions likely to occur in the title reactions is as follows:



This explains why in our reactions (runs 3, 7 and 11) only 37-44% of the starting halide remains unreacted in 35 min., when electron transfer mechanism operates using one-fourth of the equimolar quantity of LAH and also provides rationale for an earlier observation⁴³ that first hydrogen in alanate reacts more efficiently than others. In conformity with this view, we found

that the extension of the reaction time in runs 3, 6 and 9 to 240 min. indeed left lesser quantities of the unreacted halides (see Table II.2, runs 4, 8 and 12).

Intervention of free radicals has also been demonstrated in the reactions of LAH with Z-2-chlorostilbene. The reactions were carried out by the addition of LAH contained in THF to a solution of Z-2-chlorostilbene in the same solvent at ambient temperature under dry nitrogen atmosphere. The reactions proceeded with the evolution of hydrogen gas. The results are summarized in Table II.3.

Table II.3. Reaction of Z-2-Chlorostilbene (0.01 mol) with LAH in dry THF at 25°C

Run	LAH mol	Time hr	% Yield of Products			H ₂ ^a ml
			Phenanthrene	<u>Z</u> -Stilbene	<u>E</u> -Stilbene	
1	0.00625	12	33	16	nil	20
2	0.0125	12	65	30	nil	32
3	0.0125	24	66	29	nil	32
4	0.025	12	66	25	5	38
5	0.025	24	68	20	8	40
6	0.04	24	68	5	22	62
7 ^b	0.025	12	32	52	12	48
8 ^c	0.025	12	37	50	9	46

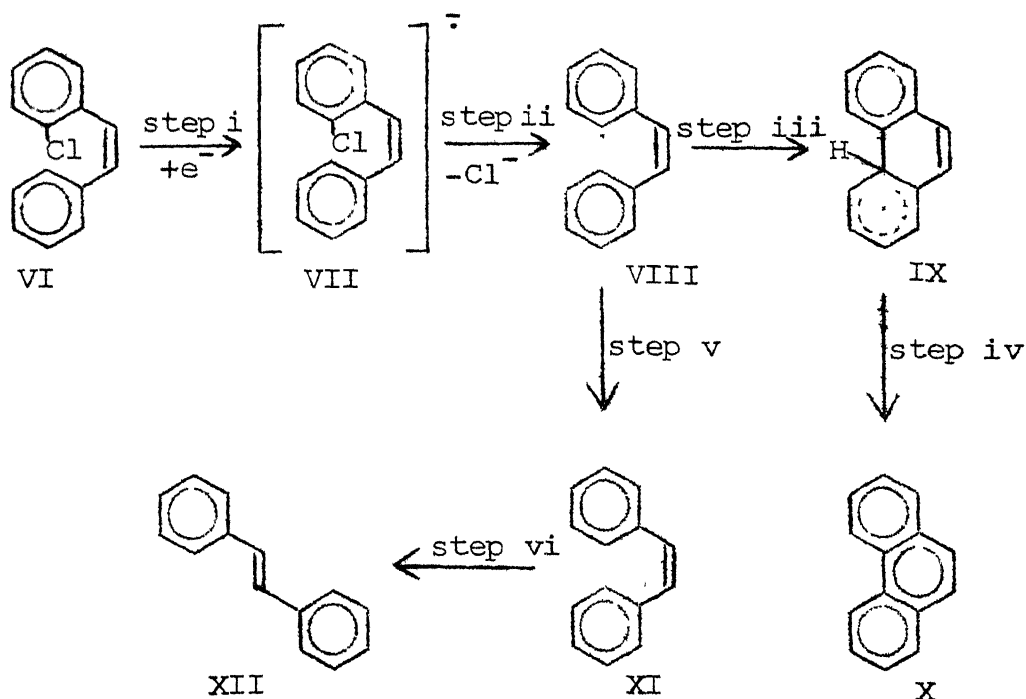
a, Volume of H₂ was determined at atmospheric pressure by comparison with control experiment in the absence of halide using same batch of reactants and solvent under identical conditions.

b, In presence of cyclohexene (0.15 mol).

c, In presence of cumene (0.15 mol).

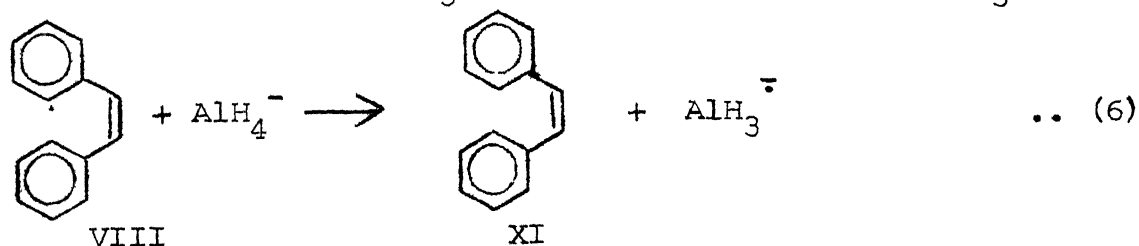
It is evident from these data that phenanthrene (X) and Z-stilbene (XI) are formed first and E-stilbene (XII) arises from the latter in a secondary process involving LAH. A comparison of the combined yields of Z- and E-stilbenes with those of phenanthrene in runs 2-6 reveals that the reductive cyclization predominates over the simple dechlorination process; but this trend is reversed in runs 7 and 8 where cyclohexene and cumene, respectively, are present. The reported⁴⁷ order of reactivities in the LAH reduction of halobenzenes i.e., $I > Br > Cl > F$, is the same as that observed⁴⁸ in electron transfer reductions using several different electron donor reagents. All these observations become discernible when intervention of radicals formed by dissociative electron capture on Z-2-chlorostilbene (VI) is considered significant as shown in the Scheme II.3.

SCHEME II.3



Conditions favoring electron transfer from LAH^{49,5} to VI in step (i) do exist in the present study. The extended conjugation in VI presumably provides ABMO of low enough energy for acceptance of an electron from LAH made available from AlH_4^- or the hydride anion ($\text{AlH}_4^- \rightleftharpoons \text{AlH}_3 + \text{H}^-$). The radical-anion VII dissociates to give radical VIII and the chloride anion. The radical VIII is known⁵⁸ to prefer intramolecular phenylation (giving X) over hydrogen atom abstraction. The favorable distance⁵⁹ of the order of 1.5 Å between the two positions to be linked in radical VIII significantly contributes to cyclisation. Evidently, the life-time of radical VIII must be long compared to the time of rotation or oscillation of the rings. However, enhanced yields of stilbenes in runs 7 and 8 reflect the known⁶⁰ ease of hydrogen atom donation by cyclohexene and cumene, respectively, to aryl radicals. The carbanion corresponding to radical VIII, even if formed would not have cyclised.⁶¹

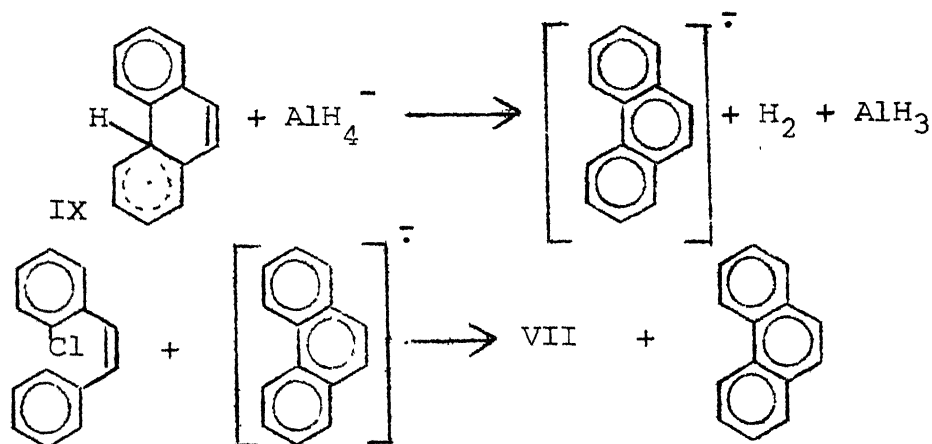
Electron donation by LAH, as seen from the volume of hydrogen gas evolved, generates only a fraction of the total amount of VIII that actually produces X, XI and XII. It is, therefore, considered likely that besides reacting by step (iii), radical VIII picks up a hydrogen atom^{49,50} from AlH_4^- producing XI and radical-anion AlH_3^- (Eq. 6). Once formed, AlH_3^- intervenes



as electron donor in step (i) which continues giving VIII as long as both Z-2-chlorostilbene and AlH_4^- are present. Consequently, Eq. 6 must account for a major portion of stilbenes obtained in runs 1-6. To confirm the aforesaid view the reaction (run 3) was repeated using LiAlD_4 instead of LiAlH_4 which yielded phenanthrene (65%) and Z-stilbene (28%) which contained largely the monodeuterated component (nmr).

The AlH_4^- present in the medium may pick up a proton from radical IX obtained by intramolecular cyclisation of radical VIII giving phenanthrene radical-anion which can then transfer the

SCHEME II.4



additional electron to Z-2-chlorostilbene producing radical-anion VII and phenanthrene (Scheme II.4).

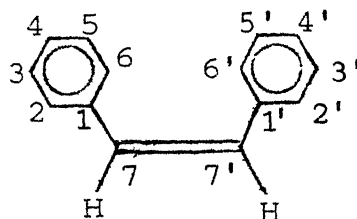
That E-stilbene is produced by LAH induced isomerisation of Z-stilbene is evident from a comparison of the yields of the two stilbenes in runs 4-8 with those in runs 1-3. This conclusion receives support from the following results obtained

by reacting an authentic sample of Z-stilbene (0.01 mol) with LiAlH_4 in 50 ml of THF at 25°C under nitrogen atmosphere for 24 hr:

LiAlH_4 , mol	: 0.005	0.01	0.02	0.05	0.10
Yield of XII, %	: 50	55	80	93	96

This isomerisation may take place by rotation about the $\text{C}_7\text{-C}_{7'}$ bond during radical-anion (formed when Z-stilbene accepts an electron) or dianion (formed when the radical-anion of Z-stilbene accepts another electron) stage of the substrate.

Formation of dianion may also be visualized through disproportionation of the radical-anion. Although disproportionation appears to be highly unfavorable owing to the large



repulsion energy between the two adjacent anionic centres in the dianion while the entropy of the system virtually remains unaltered, it may take place because the solvation energy of dianion is twice as large as that of the radical-anion.⁶²

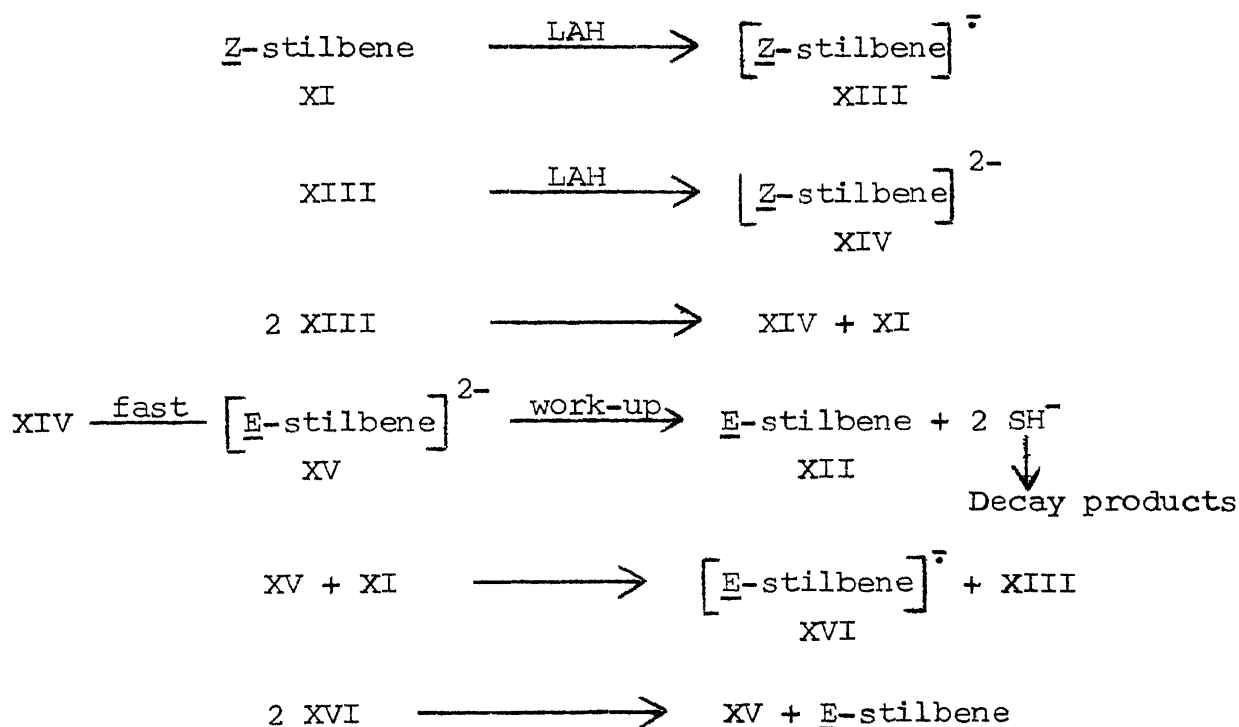
Table II.4 shows that the bond order in stilbene dianion is reduced considerably making rotation about $\text{C}_7\text{-C}_{7'}$ bond a relatively more facile process. This argument coupled with the fact that the benzyl radical accepts an electron to give benzyl anion⁶⁴ suggests that the mechanism of isomerization of Z-stilbene to E-stilbene involves rotation about the $\text{C}_7\text{-C}_{7'}$

Table II.4. Some mobile bond orders in stilbene and its mono- and dianions⁶³

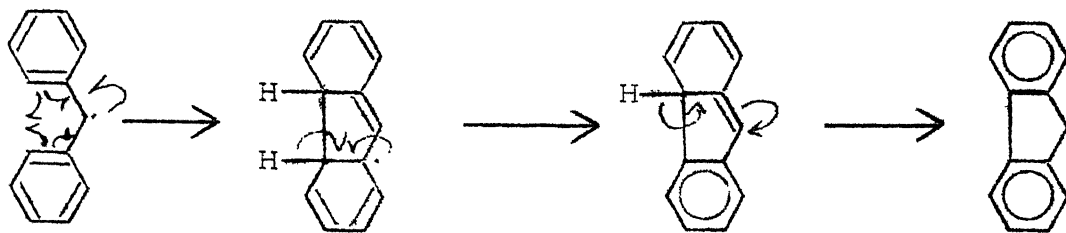
Species	Bond Orders	
	7-7'	1-7
Stilbene	0.820	0.431
Stilbene ⁻	0.628	0.526
Stilbene ²⁻	0.436	0.621

bond during the olefin's life-time as a dianion (Scheme II.5). This also explains why an excess of LAH is required to bring

SCHEME II.5



about a quantitative conversion. Formation of fluorene in the reaction of LAH with benzhydryl chloride may also be accounted for by a free radical cyclisation⁵⁶ process as shown below:



II.4 Experimental

All melting points were taken on MEL-TEMP melting point apparatus. IR spectra were recorded on Perkin-Elmer, models-137 and 521. The ESR spectra were recorded on Varian model-V-4502 EPR spectrophotometer system operating at X-band with 10 KC modulation. The NMR spectra were recorded on Varian A-60D. The products were identified by comparison of their IR spectra with those of the authentic samples, by TLC, melting points and mixed melting points. Literature melting points are cited from "Handbook of Chemistry and Physics," 50th edition, R.C. Weast (Ed.), published by Chemical Rubber Co., Cleaveland, Ohio, unless otherwise, specified.

Tetrahydrofuran (THF) was purified by keeping it over potassium hydroxide pellets overnight, refluxing over sodium wire for 5-6 hr and then distilling over sodium twice, refluxing the same for 3-4 hr with lithium aluminium hydride followed by distillation (over LAH). The distilled THF was stored in

contact with freshly drawn sodium wire.

Starting Materials

LAH (Riedel) and (SRL) of high purity were used. E-stilbene (Analar, BDH) was used as such and fluorene (BDH) was used after double recrystallisation from ethanol. Diphenyl methane (Light and Co., Colnbrook, England) was used after distillation. Silica-gel (Acme's, 100-200 mesh) was used for column chromatography. 9-Bromofluorene,⁶⁵ benzhydryl chloride⁶⁶ and 9-chloromethylantracene⁶⁷ were prepared by known procedures. 9-Methylantracene,⁶⁸ 9,9'-bifluorenylidene,⁶⁹ tetraphenylethylene,⁷⁰ Z-stilbene⁷¹ and Z-2-chlorostilbene⁷² were prepared by methods reported in the literature.

General Method for the Reduction of Halides

In a 3-necked 250 ml round bottom flask mounted over a magnetic stirring base, with a magnet inside, and connected to a nitrogen gas cylinder through a purifier, to a gas collector through a mercury trap and to a pressure equalising dropping funnel, was kept a solution of the halide (0.01 mol) in dry THF (50 ml). The halide solution was purged with nitrogen gas with continuous stirring. LAH contained in dry THF (50 ml) was added to it through the dropping funnel. After appropriate time, water was slowly added to the reaction mixture followed by the addition of dil. HCl and products extracted with five 50 ml portions of ether (unless mentioned otherwise). The combined extracts were washed with water, dried over anh. MgSO_4

and concentrated. The crude mixture so obtained was chromatographed over a silica-gel column with proper solvents as eluants to give the pure products separately.

Reaction of LAH with 9-Chloromethylantracene, Ia

(a) LAH to halide Ia molar ratio - 1:1

LAH (0.38 g, 0.01 mol) contained in 50 ml of dry THF was added to a solution of 9-chloromethylantracene (2.26 g, 0.01 mol) in 50 ml of dry THF kept at ice-bath temperature under an atmosphere of N_2 . 70 ml (63%) of hydrogen gas evolved (after accounting for the gas evolved in a control experiment) within 10 min. and a transient green color immediately appeared which faded out with time. The reaction mixture became yellow due to the formation of a yellow precipitate and was worked up by adding distilled water. The yellow precipitate obtained after filtration of the mixture and washing with water and a slight amount of hexane was identified as 1,2-di-(9-anthryl)ethane (m.p. 308-310°, lit. 308-313°C). The concentration of the ethereal extract of the filtrate gave a crude mixture which was shaken well with hexane when a part of the mixture remained insoluble and was filtered. The hexane insoluble portion was identified as 1,2-di-(9-anthryl)ethane and its total yield was 1.23 g (~64%). Hexane was removed from the filtrate and solid so obtained was recrystallised from ethanol. It was identified as 9-methylantracene (m.p. 80°, lit. 81.5°C) and amounted to 0.44 g (~23%). The compounds were characterized by comparison of IR spectra, TLC, mixed melting points and C, H analyses.

(b) LAH to halide Ia molar ratio - 1:2

Addition of LAH (0.19 g, 0.005 mol) contained in 50 ml of dry THF to a solution of 9-chloromethylantracene (2.26 g, 0.01 mol) in 50 ml of dry THF kept at ice-bath temperature under nitrogen atmosphere resulted in the evolution of 40 ml (70%) of hydrogen gas. The reaction was allowed to proceed for 35 min. after which the separation of products as detailed above yielded 9-methylantracene (0.31 g, ~16%), 9-chloromethylantracene (0.72 g, ~32%) and 1,2-di-(9-anthryl)-ethane (0.80 g, ~42%).

(c) LAH to halide Ia molar ratio - 1:4; Reaction time - 35 min.

The above reaction was repeated using LAH (0.1 g, 0.0025 mol) and 9-chloromethylantracene (2.26 g, 0.01 mol) in a total of 100 ml of THF. Hydrogen gas 21 ml (75%) was evolved. The product distribution was determined to be as 9-methylantracene (0.21 g, ~11%), 9-chloromethylantracene (1.00 g, ~44%) and 1,2-di-(9-anthryl)-ethane (0.67 g, ~35%).

(d) LAH to halide Ia molar ratio - 1:4; Reaction time - 240 min.

LAH (0.1 g, 0.0025 mol) contained in 50 ml of dry THF was added to a solution of 9-chloromethylantracene (2.26 g, 0.01 mol) in dry THF (50 ml) kept at ice-bath temperature under nitrogen atmosphere. Reaction started immediately with the evolution of hydrogen (23 ml, 82%) and was allowed to proceed for 240 min. Mixture was worked up with acidified water and the products obtained were 9-methylantracene (0.25 g, ~13%), 9-chloromethylantracene (0.81 g, ~36%) and 1,2-di-(9-anthryl)-

ethane (0.76 g, ~40%).

Reaction of LAH with Benzhydryl Chloride, Ib

(a) LAH to halide Ib molar ratio - 1:1

To a solution of benzhydryl chloride (2.02 g, 0.01 mol) in dry THF (50 ml), kept at ice-bath temperature under nitrogen atmosphere, was added LAH (0.38 g, 0.01 mol) contained in THF (50 ml). Hydrogen gas 65 ml (58%) was evolved (after accounting for the gas involved in a control experiment) within 5 minutes of the commencement of reaction and a transient yellow color developed. Reaction was allowed to proceed for 35 min. when it was worked up by the addition of water followed by dil. HCl. The ethereal extract, on concentration, gave 0.250 g of 1,1,2,2-tetraphenylethane (m.p. 212-213°C, lit. 214-215°C). Complete removal of the solvent from the mother liquor, gave a crude mixture, which on chromatography over activated silica-gel column using petroleum ether (b.p. 60-66°) and petroleum ether:benzene, 75:25 (v/v) as eluants gave diphenylmethane (0.42 g, ~25%; m.p. 26°C, lit. 26-27°C), fluorene (0.117 g, ~7%; m.p. 116°, lit. 116-117°C) and an additional 0.45 g of 1,1,2,2-tetraphenylethane. Total yield of 1,1,2,2-tetraphenylethane was 0.70 g (~42%). These compounds were identified by mixed melting points and superimposable IR spectra with those of the authentic samples.

In a separate experiment, when the reactants were mixed in the cavity of ESR spectrophotometer, strong ESR signals (not present in the pure reactants) were observed. The intensity of

these signals increased in the beginning but started decreasing after some time (Fig. II.1).

(b) LAH to halide Ib molar ratio - 1:2

Reaction was carried out by adding LAH (0.19 g, 0.005 mol) contained in dry THF (50 ml) to a solution of benzhydryl chloride (2.02 g, 0.01 mol) in dry THF (50 ml) kept at ice-bath temperature under nitrogen atmosphere. The reaction proceeded with evolution of hydrogen gas (35 ml, 63%) and the mixture was worked up after 35 min. in the usual manner. Separation of the product mixture on activated silica-gel column yielded diphenylmethane (0.22 g, ~13%), fluorene (0.083 g, ~5%), benzhydryl chloride (0.55 g, ~27%) and 1,1,2,2-tetraphenylethane (0.60 g, ~36%).

(c) LAH to halide Ib molar ratio - 1:4; Reaction time - 35 min.

LAH (0.10 g, 0.0025 mol) in 50 ml of dry THF was added to a solution of benzhydryl chloride (2.02 g, 0.01 mol) in 50 ml of dry THF kept at ice-bath temperature under nitrogen atmosphere. Hydrogen gas 20 ml (72%) evolved within 5 minutes. The reaction was allowed to proceed for 35 min. after which the mixture was worked up with acidified water and extracted with solvent ether. The products obtained on separation of the mixture using silica-gel column were diphenylmethane (0.15 g, ~9%), fluorene (0.050 g, ~3%), benzhydryl chloride (0.749 g, ~37%) and 1,1,2,2-tetraphenylethane (0.435 g, ~26%).

(d) LAH to halide Ib molar ratio - 1:4; Reaction time - 240 min.

Reduction was carried out by the addition of LAH (0.10 g, 0.0025 mol) contained in dry THF (50 ml) to a solution of benzhydryl chloride in 50 ml of THF, kept at ice-bath temperature under an atmosphere of nitrogen. Reaction was allowed to proceed for 35 min when 21 ml (75%) of hydrogen gas evolved. The reaction mixture was worked up using acidified water. The products were extracted with ether and the ethereal extract concentrated to give a mixture which was separated by means of column chromatography. Diphenyl methane (0.16 g, ~10%), fluorene (0.67 g, ~4%), benzhydryl chloride (0.6 g, ~30%) and 1,1,2,2-tetraphenylethane (0.52 g, ~31%) were obtained.

Reaction of LAH with 9-Bromofluorene, Ic

(a) LAH to halide Ic molar ratio - 1:1

LAH (0.38 g, 0.01 mol) contained in dry THF (50 ml) was added to a solution of 9-bromofluorene (2.45 g, 0.01 mol) in dry THF (50 ml) kept under nitrogen atmosphere at ice-bath temperature when 65 ml (58%) of hydrogen gas was evolved (after accounting for the gas evolved in a control experiment) within 3 min. of the commencement of reaction. A transient red color was observed. Reaction was allowed for a total of 35 min. when it was worked up by first adding water and then dil. HCl. Ethereal extract of the reaction mixture was dried over anhydrous MgSO_4 , concentrated and chromatographed over silica-gel column using petroleum ether (b.p. 60-66°) as eluant to give

fluorene (0.33 g, ~20%; m.p. 116°, lit. 116-7°C) and 9,9'-bifluorenyl (1.19 g, ~72%; m.p. 247°, lit. 247°C). Both these compounds were characterized by determining the mixed melting points and comparison of their IR spectra with those of authentic samples.

In a separate experiment when the reactants were mixed in the cavity of ESR spectrophotometer, ESR signals (not present in the pure reactants) were observed. The intensity of these signals increased with time and reached a maximum, beyond which the intensity of the ESR signal decreases (Fig. II.2).

(c) LAH to halide I_c molar ratio - 1:2

To a solution of 9-bromofluorene (2.45 g, 0.01 mol) in dry THF (50 ml), kept at ice-bath temperature under N_2 atmosphere, was added LAH (0.19 g, 0.005 mol) contained in dry THF (50 ml) when 45 ml (80%) of H_2 gas was evolved within 5 min. of the commencement of reaction. Reaction mixture was worked up in the usual manner after 35 minutes. Chromatography over activated silica-gel column with petroleum ether (b.p. 60-66°) as eluant gave fluorene (0.23 g, ~14%), 9-bromofluorene (0.735 g, ~30%) and 9,9'-bifluorenyl (0.84 g, ~51%).

(c) LAH to halide I_c molar ratio - 1:4; Reaction time - 35 min.

Addition of LAH (0.1 g, 0.0025 mol) contained in dry THF (50 ml) to a solution of 9-bromofluorene (2.45 g, 0.01 mol) in dry THF (50 ml) under N_2 atmosphere at ice-bath temperature liberated 28 ml (100%) of H_2 gas. On work up of the reaction

mixture and separation of the products by chromatography on a silica-gel column using petroleum ether (b.p. 60-66°) as eluant, fluorene (0.133 g, ~8%), 9-bromofluorene (0.98 g, ~40%) and 9,9'-bifluorenyl (0.69 g, ~42%) were obtained.

(d) LAH to halide I_c molar ratio - 1:4; Reaction time - 240 min.

To a solution of 9-bromofluorene (2.45 g, 0.01 mol in dry THF (50 ml) kept at ice-bath temperature under nitrogen atmosphere was added LAH (0.10 g, 0.0025 mol) contained in THF (50 ml) and the reaction allowed to proceed for 35 min. Hydrogen gas 28 ml (100%) was evolved. The mixture was worked up in the usual manner. Separation of the product mixture on an activated silica-gel column yielded fluorene (0.165 g, ~10%), 9-bromofluorene (0.83 g, ~34%) and 9,9'-bifluorenyl (0.76 g, ~46%).

Reaction of LAH and p-Nitrobenzyl bromide

LAH and p-nitrobenzyl bromide in dry THF were mixed in the cavity of ESR spectrophotometer. ESR spectra was recorded after 8 min. and 30 min. of the addition of reactants. Multiple line ESR signals were observed which were fairly long-lived (Fig. II.3). The intensity of these signals increased with time but started decreasing after some time.

Reaction of Fluorene with LAH: Work-up with D_2O

LAH (0.38 g, 0.01 mol) contained in 50 ml of dry THF was added to a solution of fluorene (1.66 g, 0.01 mol) in dry THF

(50 ml) kept at ice-bath temperature under nitrogen atmosphere. The mixture was stirred for 35 min. D_2O (15 ml) was added slowly to the reaction mixture and then it was worked up in the usual manner. On extraction with solvent ether and isolation, only the starting material was obtained and no deuterium incorporation was observed (nmr).

Reaction of Diphenylmethane with LAH : Work-up with D_2O

LAH (0.38 g, 0.01 mol) contained in dry THF (50 ml) was added to a solution of diphenylmethane (1.68 g, 0.01 mol) in dry THF (50 ml) kept under the same conditions as employed for the reduction of benzhydryl chloride. The mixture was worked up after stirring for 35 min., by the addition of D_2O (15 ml) followed by acidified water. On extraction and isolation, only the starting material without deuterium incorporation (nmr) was obtained.

Reaction of 9-Methylantracene with LAH: Work-up with D_2O

LAH (0.38 g, 0.01 mol) contained in dry THF (50 ml) was added to a solution of 9-methylantracene (1.92 g, 0.01 mol) under similar conditions as employed for the corresponding halide. After 35 min., D_2O (15 ml) was added to the reaction mixture and it was worked up in the usual manner. The starting material was recovered unchanged (nmr).

Reaction of 9-Chloromethylanthracene with LAH: Work-up with D₂O

LAH (0.38 g, 0.01 mol) contained in 50 ml of dry THF was added to a solution of 9-chloromethylanthracene (2.26 g, 0.01 mol) in 50 ml of dry THF kept at ice-bath temperature under nitrogen atmosphere. The reaction was worked up within 5 min. by adding 15 ml of D₂O followed by addition of acidified water. Separation of products on a silica-gel column gave 9-chloromethylanthracene (0.25 g, ~11%) with no deuterium incorporation (nmr).

Reaction of Benzhydryl Chloride with LAH: Work-up with D₂O

To a solution of benzhydryl chloride (2.02 g, 0.01 mol) in dry THF (50 ml), kept at ice-bath temperature under nitrogen atmosphere, was added LAH (0.38 g, 0.01 mol) contained in THF (50 ml). The reaction was worked up after 5 min. by adding 15 ml of D₂O followed by acidified water. Separation of products in the usual manner gave benzhydryl chloride (0.16 g, ~8%) with no deuterium incorporation (nmr).

Reaction of 9-Bromofluorene with LAH: Work-up with D₂O

Addition of LAH (0.38 g, 0.01 mol) contained in 50 ml of dry THF to a solution of 9-bromofluorene (2.45 g, 0.01 mol) in 50 ml of THF was done at ice-bath temperature under nitrogen atmosphere. The reaction was worked up within 5 min. by addition of 15 ml of D₂O followed by acidified water. Extraction, concentration and separation of products in the usual manner gave

Reaction of Tetraphenylethane with LAH

To a solution of tetraphenylethane (3.34 g, 0.01 mol) in dry THF (50 ml) was added LAH (0.38 g, 0.01 mol) contained in 50 ml of dry THF under conditions identical to that employed for the reaction of benzhydryl chloride. On working up the reaction mixture in the usual manner after 35 min., the starting hydrocarbon was recovered unchanged quantitatively.

Reaction of 9,9'-Bifluorenyl with LAH

LAH (0.38 g, 0.01 mol) contained in dry THF (50 ml) was added to a solution of 9,9'-bifluorenyl (3.30 g, 0.01 mol) in dry THF (50 ml) kept under the same conditions as employed for the reduction of 9-bromofluorene. The starting hydrocarbon was recovered unchanged quantitatively on working up the reaction mixture in the usual manner after 35 min.

Preparation of AlH_3 ⁵⁵

In a three-necked RB flask mounted over a magnetic stirring base was kept LAH (0.300 g, 0.0075 mol) and AlCl_3 (0.345 g, 0.0025 mol) in 50 ml of dry THF. The system was flushed with nitrogen and the contents of the flask allowed to stir for 60 min.

Reaction of 9-Bromofluorene with AlH_3

The flask containing AlH_3 (0.01 mol) in 50 ml of dry THF was kept at ice-bath temperature under nitrogen atmosphere and

9-bromofluorene (2.45 g, 0.01 mol) dissolved in 50 ml of dry THF was added to it. The mixture was stirred for 35 min before working up as usual. The starting halide was recovered unchanged quantitatively after extraction with ether and isolation of the products.

Reaction of 9-Bromofluorene with AlH_3 in Presence of Sodium Naphthalene

Sodium naphthalene⁵⁶ (0.0025 mol) in 15 ml of dry THF and aluminium hydride⁵⁵ (0.0075 mol) in 35 ml of dry THF were prepared in two separate flasks. A solution of 9-bromofluorene (2.45 g, 0.01 mol) in dry THF (50 ml) was added to the flask containing aluminium hydride kept at ice-bath temperature. Sodium naphthalene solution was then added to it. The green color of sodium naphthalene disappeared immediately and the reaction was allowed to proceed for 35 min. under stirring in N_2 atmosphere. The reaction mixture was worked up with acidified water as usual and the products extracted with ether. Separation of the products on a silica-gel column gave fluorene (0.183g, ~11%), 9-bromofluorene (1.06 g, ~40%) and 9,9'-bifluorenyl (0.66 g, ~40%).

Reaction of LAH with $\underline{\text{Z}}$ -2-Chlorostilbene

(a) LAH to $\underline{\text{Z}}$ -2-chlorostilbene molar ratio - 0.625:1; Reaction time - 12 hr

In a three-necked flask mounted over a magnetic stirring base and connected to a nitrogen cylinder through a purifier

and a mercury trap was placed a solution of Z-2-chlorostilbene (2.15 g, 0.01 mol) in dry THF (50 ml). Pure and dry nitrogen was passed through the solution for 10 min. LAH (0.248 g, 0.00625 mol) contained in dry THF (100 ml) was then added to the solution. The reaction commenced with the evolution of hydrogen and was allowed to proceed for 12 hr under stirring. Total volume of hydrogen gas evolved (after accounting for the gas evolved in a control experiment) was 20 ml. Reaction was worked up after slowly adding water to it. The products were extracted with ether, dried over MgSO_4 (anh.) and the solvent removed. The product mixture so obtained was chromatographed over activated silica-gel using petroleum ether (b.p. 60-66°) as eluant. Thus, Z-stilbene (0.29 g, ~16%) and phenanthrene (0.588 g, ~33%; m.p. 100°, lit. 100°C). The products were identified by mixed melting point method as well as comparison of their IR spectra with those of the authentic samples.

(b) LAH to Z-2-chlorostilbene molar ratio - 1.25:1; Reaction time - 12 hr

To a solution of Z-2-chlorostilbene (2.15 g, 0.01 mol) in THF (50 ml) under N_2 atmosphere was added LAH (0.48 g, 0.0125 mol) contained in dry THF (100 ml) and the reaction allowed to proceed for 12 hr. Hydrogen gas (32 ml) was evolved. Reaction was worked up by slow addition of water followed by extraction with ether. Separation of products using activated silica-gel column and petroleum ether (b.p. 60-66°) as eluant yielded Z-stilbene (0.54 g, ~30%) and phenanthrene (1.16 g, ~65%).

(c) LAH to Z-2-chlorostilbene molar ratio - 1.25:1; Reaction time - 24 hr

The above reaction was repeated for 24 hr under exactly similar conditions. Hydrogen gas (32 ml) was evolved. The products were separated by the same method as mentioned above. Thus, Z-stilbene (0.52 g, ~29%) and phenanthrene (1.175 g, (~66%)) were obtained.

(d) LAH to Z-2-chlorostilbene molar ratio - 2.5:1; Reaction time - 12 hr

Reduction was carried out by adding LAH (0.95 g, 0.025 mol) contained in dry THF (100 ml) to a solution of Z-2-chlorostilbene (2.15 g, 0.01 mol) in dry THF (50 ml) under N_2 atmosphere. Reaction was allowed to proceed for 12 hr when H_2 (38 ml) was evolved. Reaction was worked up in the usual manner. Separation of products on activated silica-gel column using petroleum ether (b.p. 60-66°) as eluant gave a mixture of Z- and E-stilbenes (0.54 g, 30%) and phenanthrene (1.175 g, ~66%). The yields of Z- and E-stilbenes were determined by GLC using 10 ft. long silicone rubber SE-30 column and found to be Z-stilbene, 0.45 g (~25%) and E-stilbene, 0.09 g (~5%).

(e) LAH to Z-2-chlorostilbene molar ratio - 2.5:1; Reaction time - 24 hr

The above reaction was repeated for 24 hr under otherwise similar conditions. H_2 (40 ml) was evolved. The products were analysed by the method detailed above. Thus, Z-stilbene (0.36 g, ~20%), E-stilbene (0.145 g, ~8%) and phenanthrene (1.210 g, ~68%) were obtained.

(f) LAH to *Z*-2-chlorostilbene molar ratio - 4:1; Reaction time - 24 hr

When the reaction was repeated under same conditions using LAH (1.52 g, 0.04 mol) contained in dry THF and a solution of *Z*-2-chlorostilbene (2.15 g, 0.01 mol) in dry THF for a period of 24 hr, hydrogen gas (62 ml) was evolved. The products were analysed by the usual method. Thus, *Z*-stilbene (0.09 g, ~5%), *E*-stilbene (0.396 g, ~22%) and phenanthrene (1.210 g, ~68%) were obtained.

Reaction of LAH with *Z*-2-Chlorostilbene in the Presence of an Excess of Cyclohexene; Reaction time - 12 hr

In a three-necked flask mounted over a magnetic stirring base was placed *Z*-2-chlorostilbene (2.15 g, 0.01 mol) in dry THF (50 ml) and cyclohexene (12.3 g, 0.15 mol). The system was flushed with dry nitrogen and LAH (0.95 g, 0.025 mol), contained in 100 ml of dry THF was added to the flask. Reaction was allowed to proceed for 12 hr. Hydrogen gas (48 ml) was evolved. On work up and product analysis in the usual way, the products were found to be *Z*-stilbene (0.936 g, ~52%), *E*-stilbene (0.216 g, ~12%) and phenanthrene (0.57 g, ~32%).

Reaction of LAH with *Z*-2-Chlorostilbene in the Presence of an Excess of Cumene; Reaction time - 12 hr

The above reaction was repeated using cumene (18 g, 0.15 mol) instead of cyclohexene under otherwise similar conditions. Hydrogen gas (46 ml) was evolved. *Z*-Stilbene (0.9 g, ~50%), *E*-stilbene (0.16 g, ~9%) and phenanthrene (0.66 g, ~37%) were

found by the usual method to be present in the mixture of products.

Reaction of LAD with Z-2-Chlorostilbene; Reaction time - 24 hr

Reduction was carried out using Z-2-chlorostilbene (2.15 g, 0.01 mol) in dry THF (50 ml), and LAD (0.5 g, 0.0125 mol) contained in 100 ml of dry THF. Reaction which started with gas evolution was allowed to proceed for 24 hr when it was worked up by adding water followed by dil. HCl. The products were extracted with ether, the ether extract washed with water and dried over MgSO_4 (anhydrous). The solvent was distilled off. Analysis of product mixture by the method described above in the reactions of LAH gave phenanthrene (1.15 g, ~65%) and Z-stilbene (0.5 g, ~28%). NMR spectrum of Z-stilbene obtained in this experiment indicated that approximately 85% of the hydrocarbon was monodeuterated.

Reaction of LAH with Z-Stilbene

(a) LAH to Z-stilbene molar ratio - 1:2

In a three-necked RB flask mounted over a magnetic stirring base and connected to a N_2 gas cylinder through a purifier, a mercury trap and a stopper, was placed Z-stilbene (1.8 g, 0.01 mol) in dry THF (50 ml). N_2 gas was passed through the solution for 10 min. LAH (0.19 g, 0.005 mol) contained in 200 ml of dry THF was added to it. The reaction which occurred with H_2 gas evolution was allowed to proceed for 24 hr. After

this period, water was added to the reaction mixture followed by dil. HCl. The reaction mixture was extracted with ether, extract washed with water and dried over MgSO_4 (anhyd.). The solvent was then removed by distillation. Analysis by quantitative UV spectroscopy using methanol as solvent and VPC on a 10 ft. silicone rubber SE-30 column following calibration method established the presence of Z-stilbene (0.9 g, ~50%) and E-stilbene (0.9 g, ~50%) in the product mixture.

(b) LAH to Z-stilbene molar ratio - 1:1

The above reaction was repeated using Z-stilbene (1.8 g, 0.01 mol) and LAH (0.38 g, 0.01 mol) under otherwise similar conditions. Product distribution was determined by VPC using the same column when Z-stilbene (0.81 g, ~45%) and E-stilbene (0.99 g, ~55%) were indicated.

(c) LAH to Z-stilbene molar ratio - 2:1

This reaction with new molar ratio of the reactants (using 1.8 g, 0.01 mol of Z-stilbene) was conducted along the same lines as described above. After work-up and analysis by VPC using 10 ft. silicone rubber SE-30 column, the product mixture was found to contain Z-stilbene (0.36 g, ~20%) and E-stilbene (1.44 g, ~80%).

(d) LAH to Z-stilbene molar ratio - 5:1

The reaction of Z-stilbene (1.8 g, 0.01 mol) with five times the molar quantity of LAH was conducted in the same way

as the above experiments. After stirring for 24 hr, the mixture was extracted with ether and products analysed by VPC as usual. Thus, presence of Z-stilbene (0.126 g, ~7%) and E-stilbene (1.674 g, ~93%) in the product mixture was established.

(e) LAH to Z-stilbene molar ratio - 10:1

The above reaction was conducted using Z-stilbene (1.8 g, 0.01 mol) and ten times the molar quantity of LAH under otherwise same conditions for 24 hr. The product mixture, on analysis, in the usual way, was found to contain Z-stilbene (0.072 g, ~4%) and E-stilbene (1.728 g, ~96%).

II.5 References

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CHAPTER III

ELECTRON TRANSFER IN THE DITHIONITE REDUCTIONS OF BENZYLIC HALIDES

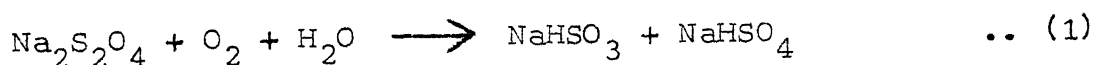
III.1 Abstract

Reactions of 4-nitrobenzyl bromide, 9-bromofluorene, benzhydryl chloride and 9-chloromethylantracene with sodium dithionite were studied in dry dimethylformamide (DMF) at reflux temperature (155-160°) in an atmosphere of nitrogen in order to elucidate the reaction path. Sulfur dioxide gas evolution took place in all these reactions. Each halide - (Ar-CH-X) gave the dimeric product Ar-CH-CH-Ar. While 4-nitrobenzyl bromide, 9-bromofluorene and 9-chloromethylantracene also gave the corresponding dehalogenation product (Ar-CH₂), benzhydryl chloride yielded fluorene. Olefinic dimers (Ar-C=C-Ar) were also obtained in the cases of the former two halides and perhaps with 9-chloromethylantracene. A sulfone, Ar-CH-SO₂-CH-Ar, was isolated among the products of the reaction of 4-nitrobenzyl-bromide. A mechanism initiated by transfer of an electron from the sulfur dioxide radical-anion (SO₂⁻) to the halide in which

the benzylic radicals intervene has been proposed. We found that the sulfone is formed via coupling between a benzylic radical and the sulfinate anion and also that carbanions are involved in the formation of the dehalogenation products $(\text{Ar}-\underset{\downarrow}{\text{CH}_2})$ as well as the olefinic dimers $(\text{Ar}-\underset{\downarrow}{\text{C}}=\underset{\downarrow}{\text{C}}-\text{Ar})$. Dimers $(\text{Ar}-\underset{\downarrow}{\text{CH}}-\underset{\downarrow}{\text{CH}}-\text{Ar})$ are produced as a result of radical coupling. Benzhydryl radicals cyclize to give fluorene.

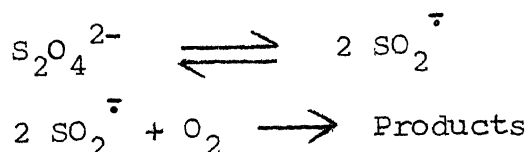
III.2 Introduction

Sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$, is a powerful reducing agent. Besides being a useful laboratory reagent, it is also widely used in industry. The reagent is relatively inexpensive and conveniently employed for reductions in aqueous media^{1,2} - often in the presence of an excess of sodium bicarbonate in order to keep the reaction mixture basic - or in combination with organic solvents like dimethylformamide (DMF), methanol, ethanol, dioxane etc. Because of its tendency to reduce oxygen efficiently at room temperature, it is used as a reagent in the purification of nitrogen gas. The chemical reaction is outlined in Eq. (1):



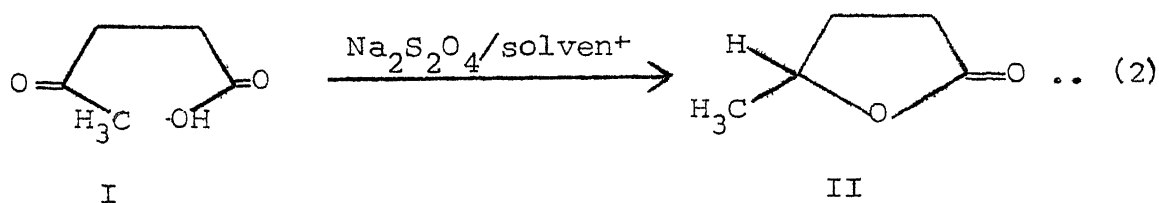
Kinetic studies³⁻⁶ have indicated that the dithionite reduction of oxygen takes place by a two-step process (Scheme III.1):

SCHEME III.1

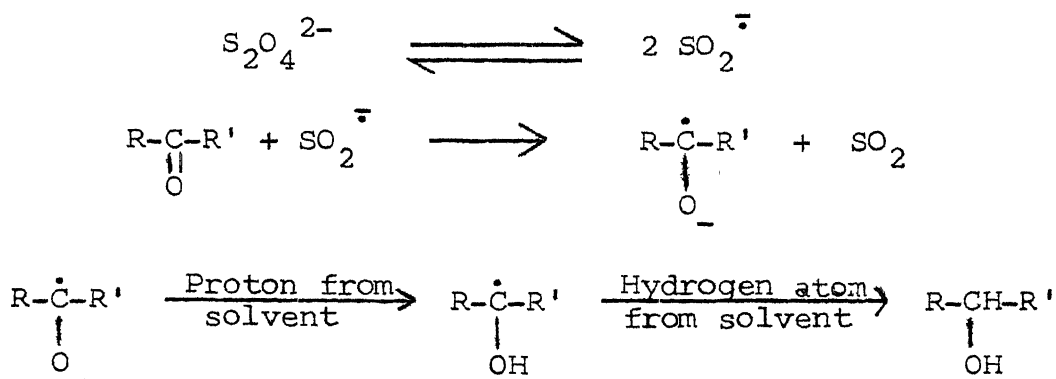
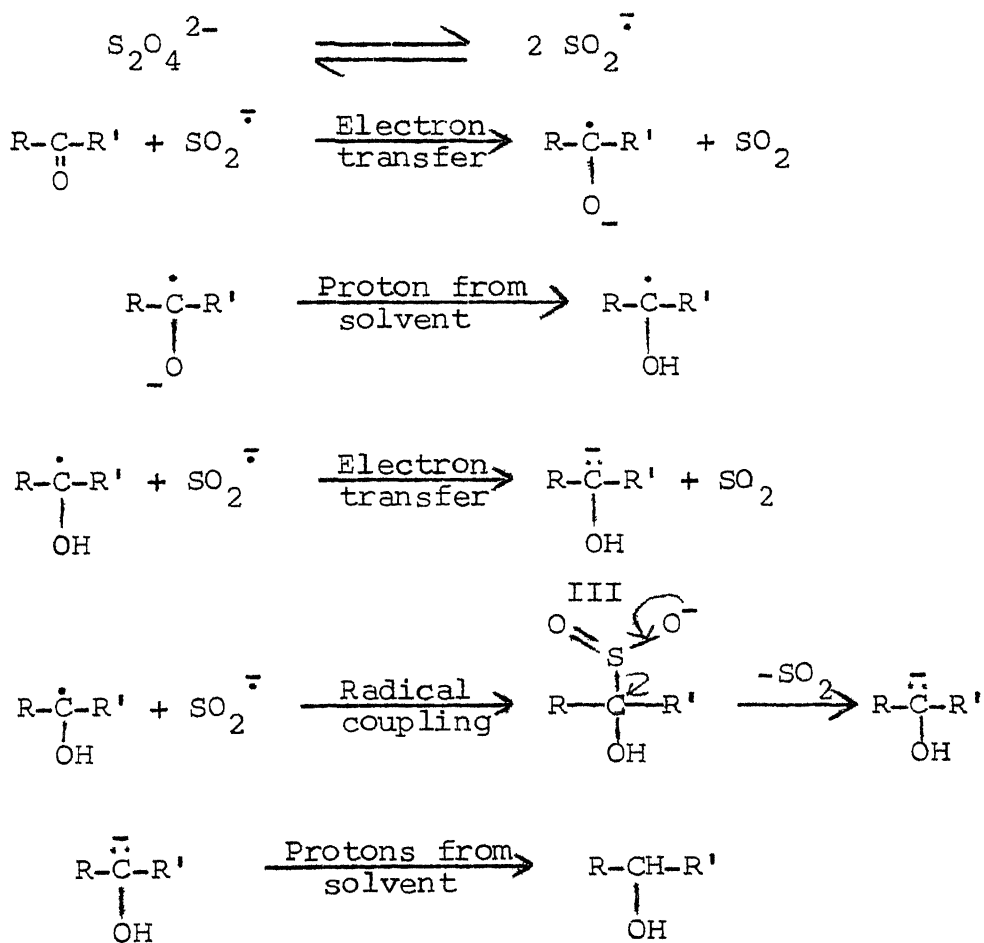


Sodium dithionite also reduces hydrogen peroxide and the hydroperoxide anion (HO_2^-).⁶

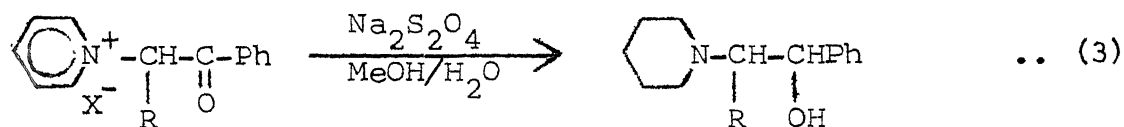
In organic chemistry, sodium dithionite has been used to reduce a variety of functional groups. For example, it reduces benzil to benzoin⁷ and carbonyl compounds to the corresponding monohydric alcohols.¹ Carboxylic acids and amides are not reduced by this reagent whereas esters and nitriles are hydrolysed. Thus, on treatment of methyl benzoate with sodium dithionite, benzoic acid (84%) was obtained.⁸ The reduction of levulinic acid (I) as shown in Eq. (2) provides an example of a selective transformation to the lactone (II):



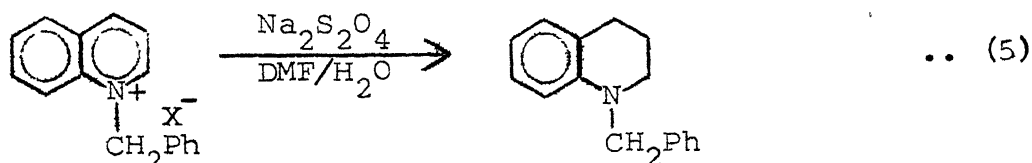
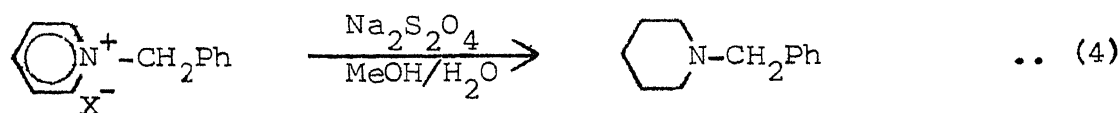
Here, dithionite appears to preferentially reduce the carbonyl group situated adjacent to the methyl group, to monohydric alcohol which undergoes intramolecular dehydration yielding the lactone (II). Reduction of the carbonyl group can take place by either of the pathways shown in Schemes III.2 and III.3: Intermediate (IV) is a sulfinic anion. Since experimental data are not available, none of the possibilities outlined above can be ruled out. Recently, de Vries and Kellogg^{1b} have also suggested the latter possibility.

SCHEME III.2SCHEME III.3

Pyridinium and quinolinium salts are reduced⁸ by sodium dithionite to piperidines and tetrahydroquinolines, respectively, as indicated in Eqs. (3-5):

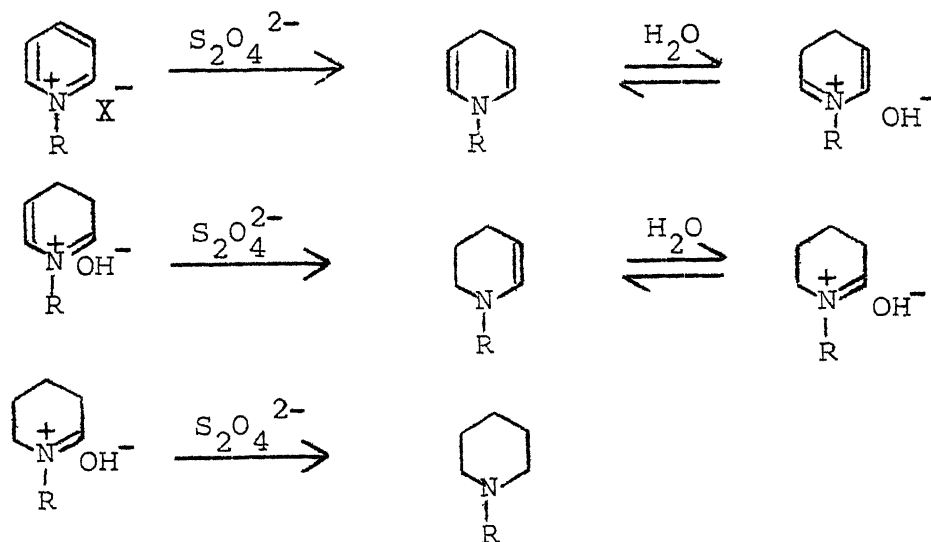


R = -COPh, -H



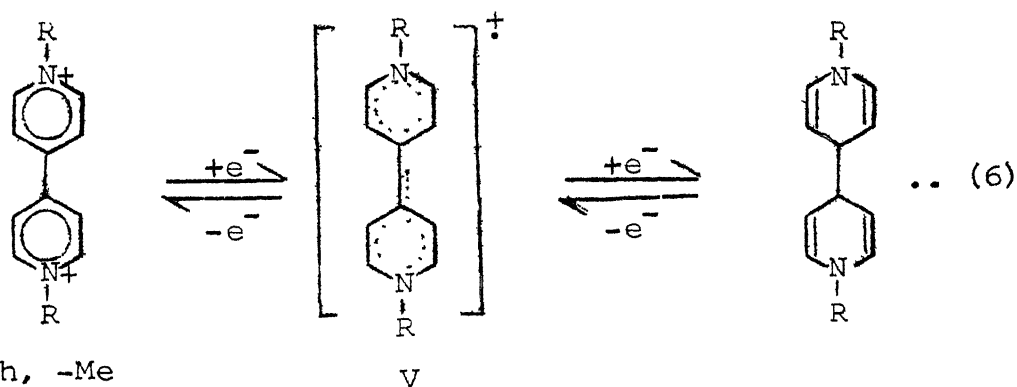
The steps postulated⁸ for the above mentioned reactions are shown in Scheme III.4:

SCHEME III.4



This stepwise reduction is presumably initiated by the addition of an electron from $\text{SO}_2^{\cdot-}$ to the pyridinium cation. The radical thus formed either accepts another electron from a second $\text{SO}_2^{\cdot-}$ species or undergoes radical coupling with $\text{SO}_2^{\cdot-}$ followed by loss of SO_2 yielding in both cases, an anion which on protonation gives the dihydro compound (see Scheme III.3).

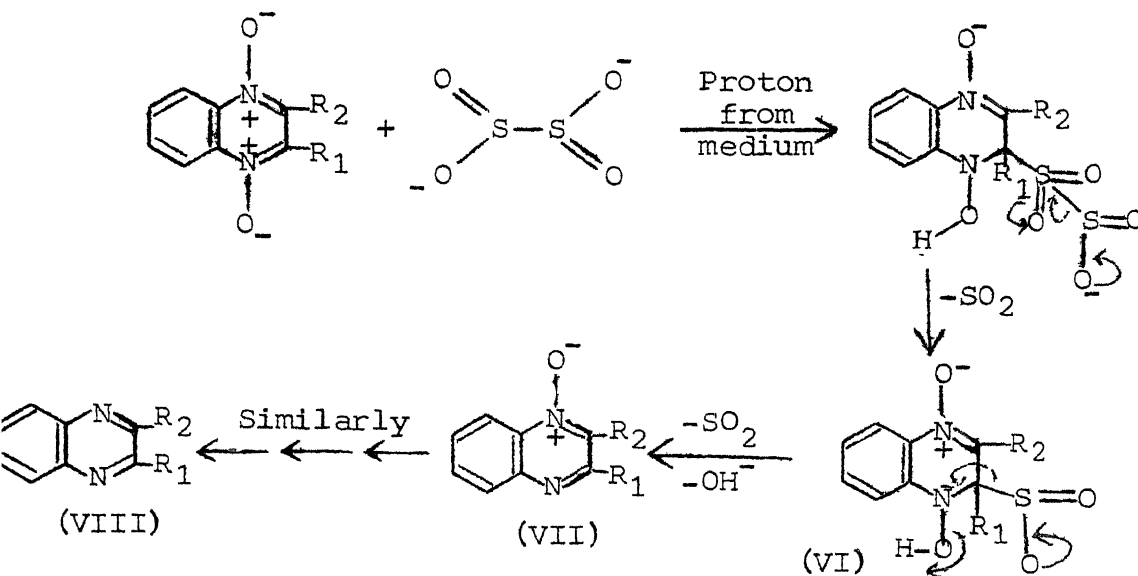
Dithionite reduction of viologens^{2,9} involves two distinct one-electron reduction steps as shown in Eq. (6). The first step produces a deep violet radical-cation (V) and the second



reduction step forms a neutral, red 1,1'-dialkyl-1,1',4,4'-tetrahydro-4,4'-bipyridyl.

Sodium dithionite brings about deoxygenation of aromatic N-oxides.⁷ The yield of the reduction products vary with the quantity of the reagent used. Optimum yield was obtained with 4:1 molar ratio of dithionite to the N-oxide. The mechanism of this reaction is believed to be that outlined in Scheme III.5:

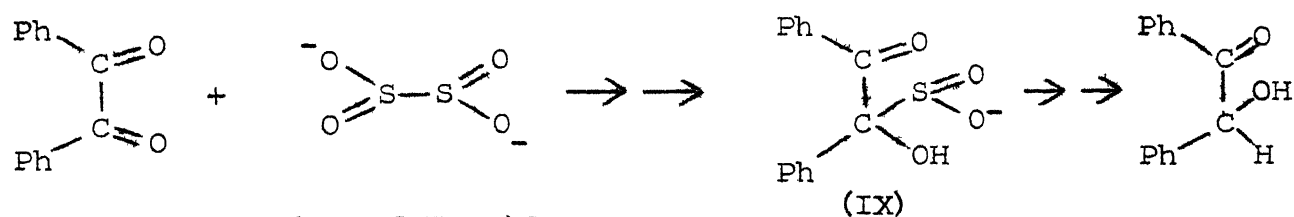
SCHEME III.5



The first step of this mechanism is the nucleophilic attack by dithionite at position 2 (or 3) of the 1,4-dioxide. The resulting intermediate is postulated to lose SO₂ giving the sulfinate anion (VI) which undergoes decomposition in a manner analogous to the decarboxylation of β -hydroxycarboxylate anions, yielding the mono-oxide (VII). Repetition of the same sequence of bond formation and bond cleavage processes on (VII) gives rise to the completely deoxygenated product (VIII).

Affinity of the dithionite for nucleophilic attack at electrophilic centre or electron donation to acceptor substrates is also indicated by the ease with which it reduces benzil to benzoin⁷ (Scheme III.6) under conditions similar to those used

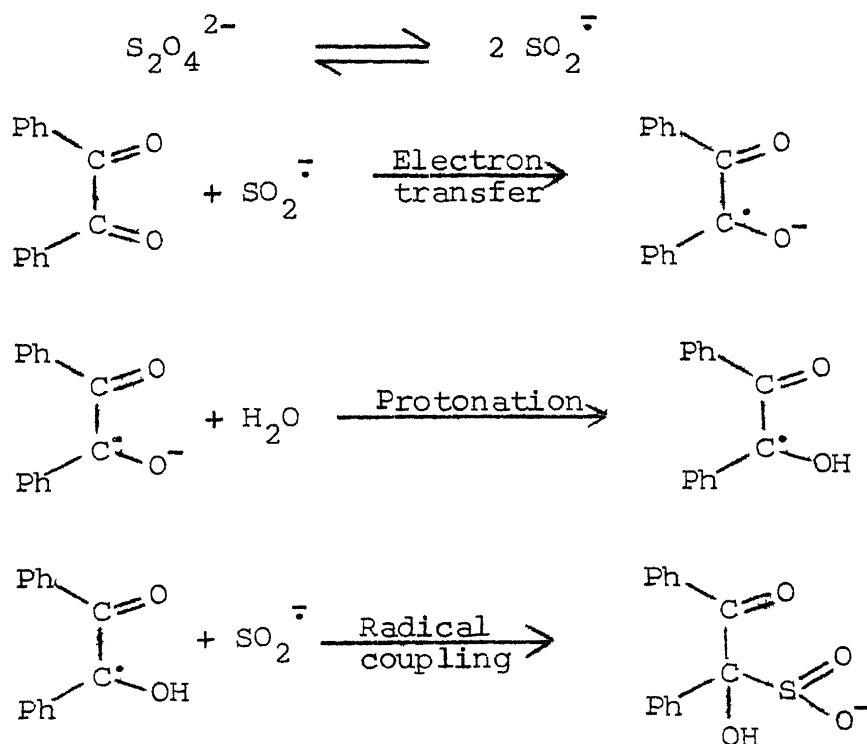
SCHEME III.6



for deoxygenation of N-oxides.

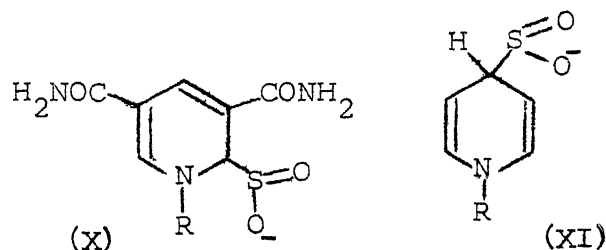
The reduction of quinones to hydroquinones by dithionite¹⁰ appears to be closely related to the above mentioned reactions. In our view, however, the formation of intermediate sulfinic anions (VI) and (IX) in Schemes III.5 and III.6, respectively, can also be visualized to be taking place through single electron transfer from $\text{SO}_2^{\cdot -}$ to the substrate. For example, sulfinic anion intermediate (IX) might arise by electron transfer followed by protonation and radical coupling reactions outlined in Scheme III.7:

SCHEME III.7



The potential of alcohol dehydrogenases for effective stereospecific and selective oxidation-reduction reactions as

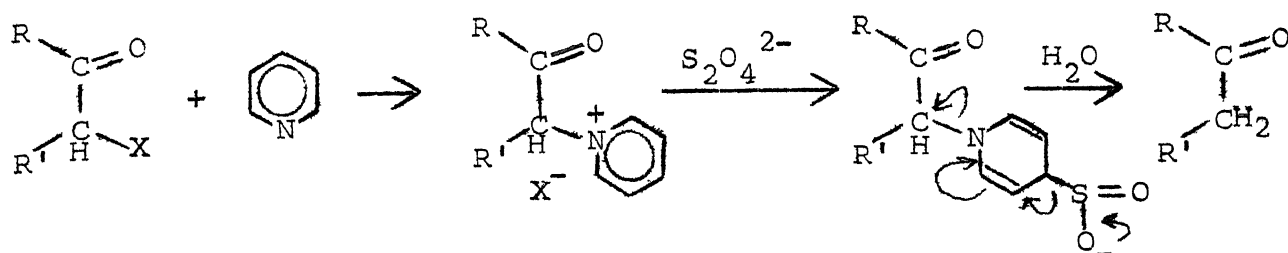
applied to biological systems¹¹ has been exploited to a limited extent in preparative organic chemistry, presumably because the required coenzymes are highly expensive. But, chemical recycling of the coenzyme could be an attractive possibility. In this connection it has been observed that sodium dithionite is very effective in the quantitative, 1,4-reduction of NAD to NADH while full enzymic activity is retained. Although intermediates (X) and (XI) have been isolated^{12,13} during the reduction of



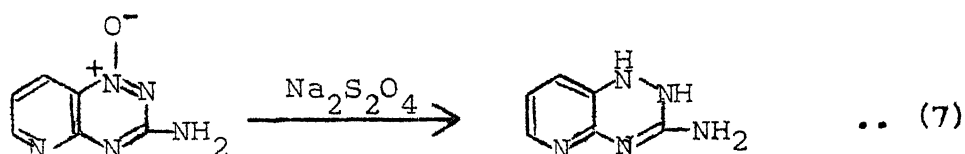
pyridinium compounds with dithionite, elimination to fully aromatic products in the cases under consideration occurs much too rapidly to permit isolation of an analogous intermediate presumed to be involved here.

The tendency of a halogen in α -haloketones to undergo nucleophilic displacement by pyridine, coupled with the observation concerning facile reduction of pyridinium salts by dithionite to 1,4-dihydropyridine derivatives has led to the development of a new procedure for dehalogenation¹⁴ as shown in Scheme III.8:

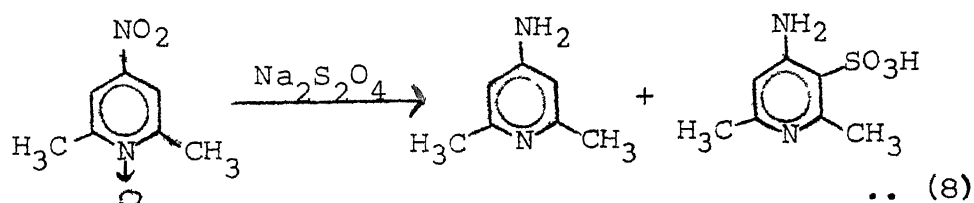
SCHEME III.8



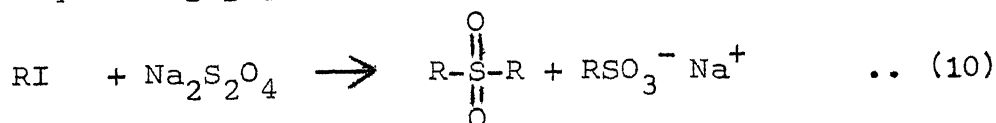
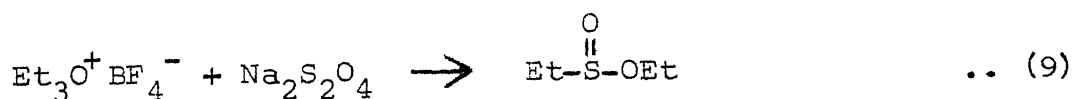
Not only can sodium dithionite remove the N-oxide function but also reduce the unsaturated bonds simultaneously as exemplified by the reduction of a cyclic triazine-N-oxide¹⁵ (Eq. 7):



Evans and Brown¹⁶ have reported the concurrent reduction of a nitro group and N-oxide function in the case of 4-nitro-2,6-lutidine-1-oxide (Eq. 8):



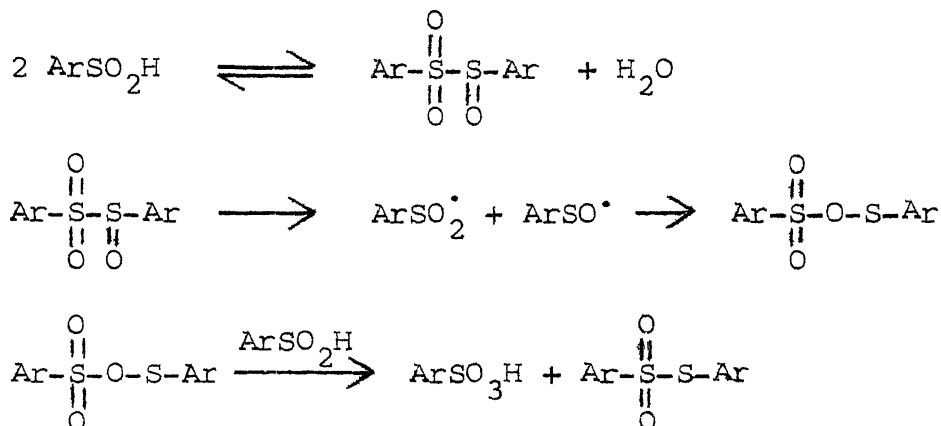
The alkylation of sodium dithionite may result in the formation of S-alkylated and O-alkylated products owing to its ambident nature. Whereas powerful alkylating agent triethyl-oxonium fluoborate ($\text{Et}_3\text{O}^+ \text{BF}_4^-$) attacks oxygen atoms (Eq. 9), weaker alkylating agents like alkyl iodides and trimethylsulfoxonium iodide ($\text{Me}_3\text{S}^+ \text{OI}^-$) attack only the sulfur atoms¹⁷ as shown in Eqs. (10-11):



(R = Me, Et)

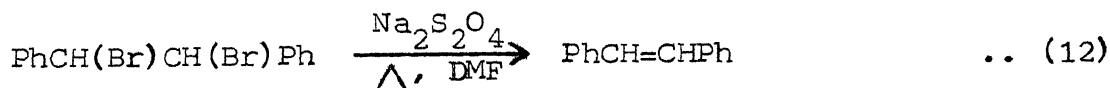
to give another intermediate (XIII) in a manner analogous to the one reported earlier by Kice and coworkers¹⁸ for the rearrangement of aryl sulfinic acids to aryl sulfonic acids and diaryl sulfinyl sulfones as outlined in Scheme III.11.

SCHEME III.11

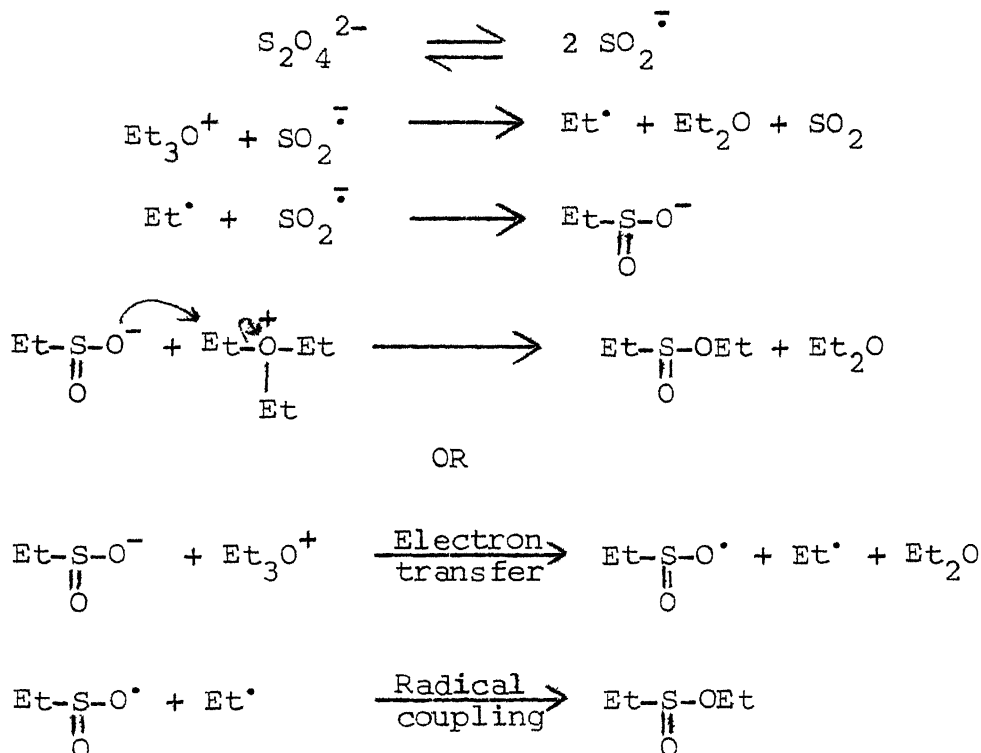


Based on the radical mechanism (Scheme III.11) proposed by Kice and coworkers and the fact that dithionite exists in equilibrium with the sulfur dioxide radical anion ($\text{SO}_2^{\bullet -}$)^{3,19} we believe that O-alkylation which has been postulated to be taking place through purely nucleophilic displacement or a four centred cyclic transition state (Scheme III.9), can also be explained through radical intermediates as shown in Scheme III.12.

Sodium dithionite has been found to be an effective debrominating agent for 1,2-dibromides²⁰ in refluxing DMF (Eq. 12):

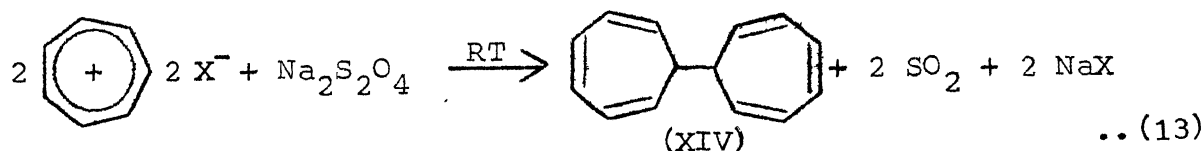


SCHEME III.12

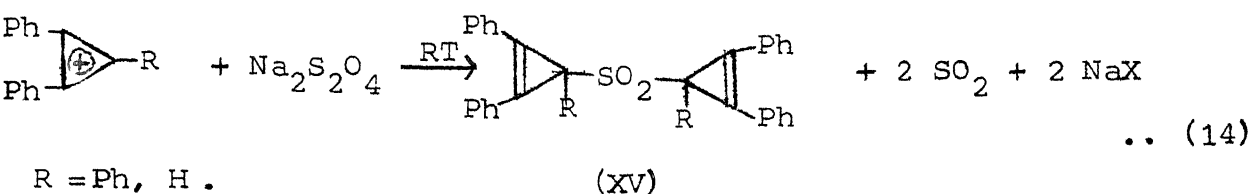


The possibility of a nucleophilic attack by the SO_2^- species on an intermediate carbocation derived from the vicinal dibromide or alternatively, a single electron transfer process has been indicated by the authors.²⁰

Dithionite reduction of tropylium cation at room temperature gives quantitative yield of ditropyl²¹ (Eq. 13); but when

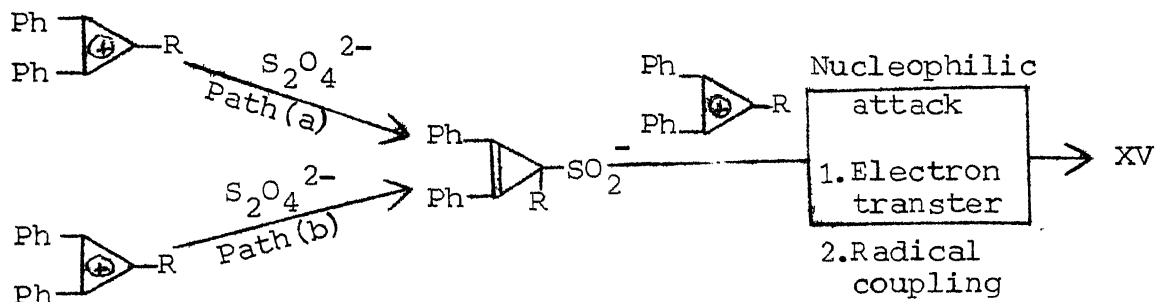


the reductive coupling on a cyclopropenium salt was attempted, the product was dicyclopropenyl sulfone as shown in Eq. (14):



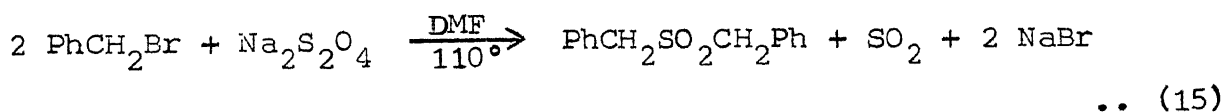
Whereas the former reaction is dimerisation of tropenyl (cycloheptatrienyl) radicals the latter presumably involves either an ion association or a combination of cyclopropenyl radical with a SO_2^\cdot to yield the sulfinate anion which attacks another unit of cyclopropenium cation or transfers an electron to the latter followed by radical coupling yielding the sulfone (Scheme III.13):

SCHEME III.13



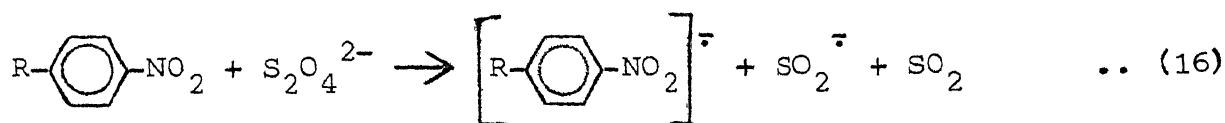
Path (a) = Nucleophilic attack followed by loss of SO_2 .
 Path (b) = Electron transfer and radical coupling.

Benzyl bromide on being heated with dithionite in DMF at 110° , yielded 17% of dibenzyl sulfone²² as shown in Eq. 15:



The reaction presumably involves a mechanism analogous to the one outlined in Scheme III.13.

Kolker and Waters²³ have observed that parasubstituted nitrobenzenes, on treatment with aqueous dithionite, yield radical-anions having sufficiently long life-time for investigation by ESR method. Many of the spectra show an ESR signal attributed to the radical-anion of sulfur dioxide ($\text{SO}_2^{\cdot -}$). Such a radical-anion, derived from dithionite, must clearly act as a single electron reducing agent (Eq. 16):



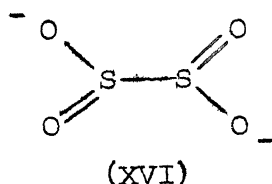
The radical-anion of sulfur dioxide so produced in the medium may also act as a source of electron.

The reduction of a variety of carbonyl compounds^{1,8,25} with dithionite gives monohydric alcohols. The kinetics of the reduction by dithionite²⁴ of biochemically interesting substances like ferricytochrome C and lumiflavin 3-acetate etc. indicate the involvement of radical-anion intermediates.

Despite the fact that sodium dithionite is readily available and easy to handle, one is struck at the sparseness of reports concerning its chemistry. In view of the possible mechanistic variations in the reactions of dithionite ion discussed above, we decided to study the mode of its action on a few benzylic halides the reactions of which with some other reducing agents are rather well understood.

III.3 Results and Discussion

It is known²⁶ that the dithionite anion (XVI) has a S-S bond length of 2.39 Å which is larger than the distance found in typical disulfides and polysulfides. The dianion is

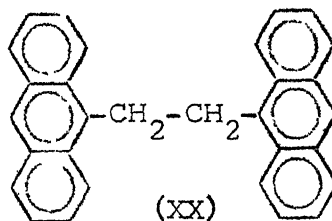
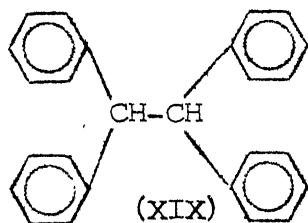
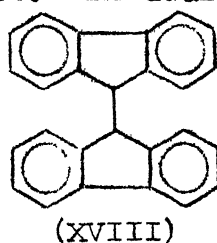
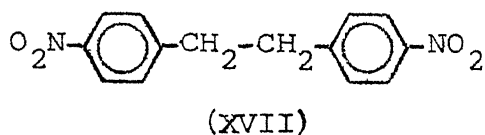


non-planar, the angle between the planes of SO₂ groups being 30°, and the order of the S-S bond corresponds to a (Pauling) bond-order of only about one-third.²⁶ Due to this weak bond, it has a tendency towards dissociating into two units of sulfur dioxide radical-anion (SO₂^{•-}). The existence of SO₂^{•-} species,¹⁹ in solid and solution phases, has been confirmed by ESR studies. While dithionite anion should be capable of initiating a nucleophilic attack at electrophilic centres under various conditions, at higher temperatures its reactions are known to yield radical-anions, protonated radicals or anions as intermediates.²⁵

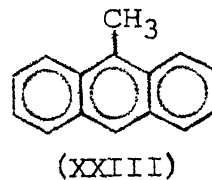
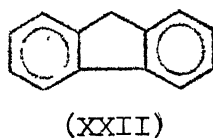
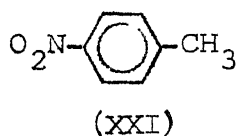
In order to examine the behavior of dithionite towards benzylic halides, we carried out reactions of 4-nitrobenzyl bromide, 9-bromofluorene, benzhydryl chloride and 9-chloromethylantracene with sodium dithionite in dry dimethylformamide (DMF) at 155-160°C (refluxing) under an atmosphere of nitrogen. In all the four cases, reactions started with fast evolution of SO₂ gas (tested by passing into K₂Cr₂O₇ solution), while SO₂ evolution was negligible after a period

of 10 min. with 9-bromofluorene, benzhydryl chloride and 9-chloromethylantracene, slow gas evolution continued upto ca. 35 min. in the case of 4-nitrobenzyl bromide. In all cases, the reaction mixtures were cooled to room temperature after one hour and then worked up by adding water acidified with hydrochloric acid.

On product analysis, each benzylic halide - $\text{Ar}-\underset{|}{\text{CH}}-\text{X}$, was found to have yielded a dimer - $\text{Ar}-\underset{|}{\text{CH}}-\underset{|}{\text{CH}}-\text{Ar}$ (cf. compounds XVII, XVIII, XIX and XX) as the major product. In addition,

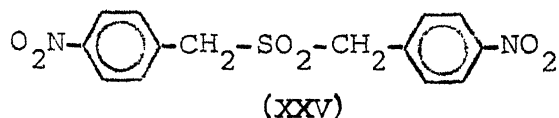
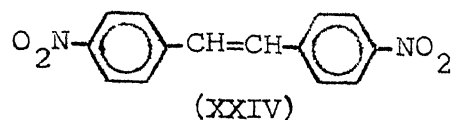


dehalogenated products, $\text{Ar}-\underset{|}{\text{CH}}_2$ (i.e., XXI, XXII and XXIII) were obtained in low yields with 4-nitrobenzyl bromide,



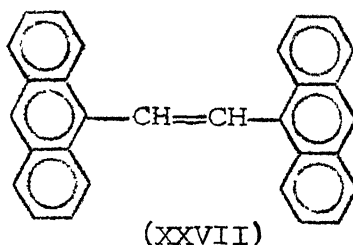
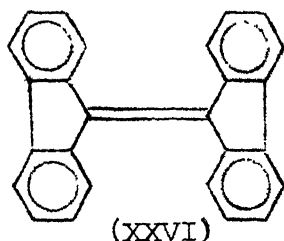
9-bromofluorene and 9-chloromethylantracene. Benzhydryl chloride, instead of giving diphenylmethane, yielded a small amount (3%) of fluorene (XXII). The other products identified

in these reactions were 4,4'-dinitrostilbene (XXIV) and di-(4-nitrobenzyl) sulfone (XXV) in the case of p-nitrobenzyl bromide;



and bifluorenylidene (XXVI) in the case of 9-bromofluorene.

A compound presumably, 1,2-di-(9-anthryl)-ethylene (XXVII), observed on tlc plate could not be isolated (being in very low yield) in the reaction involving 9-chloromethylanthrane.



These results are summarised in Table III.1.

We recall here that in its reactions, the dithionite anion can act as a nucleophile or an electron donor reagent. While acting as a nucleophilic reagent, it may undergo O-alkylation with powerful alkylating agents.¹⁷ whereas the total absence of any O-alkylation products in our reactions is indicative of non-existence of powerful alkylating agents like carbocations - $\text{Ar}-\overset{+}{\text{C}}\text{H}_2$, the formation of di-(4-nitrobenzyl)-sulfone (XXV) in the reaction of at least one halide viz. 4-nitrobenzyl bromide demonstrates S-alkylation.

Table III.1. Reactions of Benzylic Halides, $\text{Ar}-\underset{|}{\text{CH}}-\text{X}$ (0.01 mol) with Sodium Dithionite in DMF at 155-160° for one hr.

Reaction No.	Halide	Molar ratio Halide/ $\text{Na}_2\text{S}_2\text{O}_4$	Products ^{a,b}		% Yield	
			A	B	C	D
1	4-Nitrobenzyl bromide	1:1.5	25	14	6	52
2	4-Nitrobenzyl bromide	1:0.5	33	7	3	43
3	9-Bromo-fluorene	1:1.5	73	12	6	-
4	9-Bromo-fluorene	1:0.5	80	8	3	-
5	Benzhydryl chloride ^c	1:1.5	81	-	-	-
6	9-Chloromethylanthracene	1:1.5	78	5	trace ^d	-

A = $\text{Ar}-\underset{|}{\text{CH}}-\underset{|}{\text{CH}}-\text{Ar}$; B = $\text{Ar}-\underset{|}{\text{CH}}_2$; C = $\text{Ar}-\underset{|}{\text{C}}=\underset{|}{\text{C}}-\text{Ar}$;
D = $\text{Ar}-\underset{|}{\text{CH}}-\text{SO}_2-\underset{|}{\text{CH}}-\text{Ar}$.

a. SO_2 gas was evolved in all the reactions.

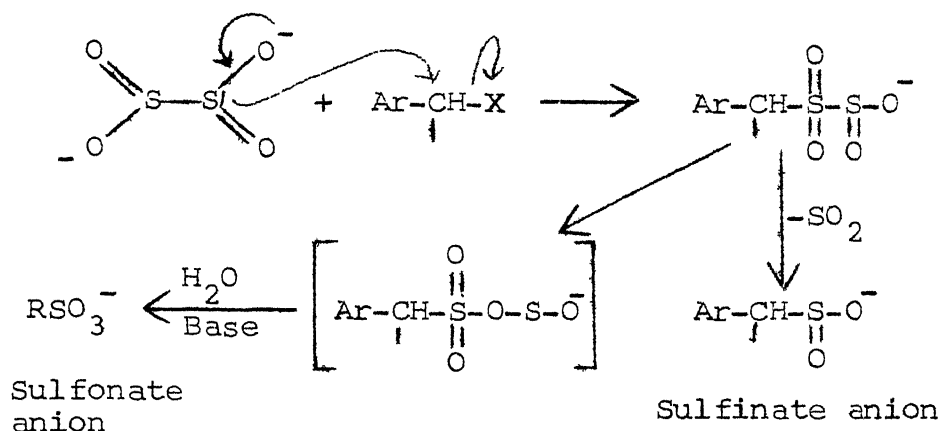
b. Reactions of the halides also indicated the presence of the corresponding aldehydes and alcohols in yields varying between 1-3% as in the blank experiment.

c. Fluorene (3%) was obtained as an additional product.

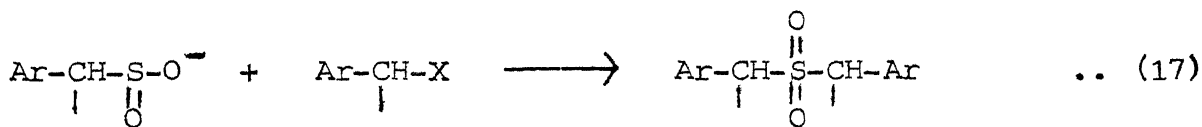
d. TLC showed a spot corresponding to 1,2-di-(9-anthryl)-ethylene which could not be separated.

One of the conceivable pathways for S-alkylation leading to the formation of a sulfinate anion involves nucleophilic attack by the dithionite anion.¹⁶ In this mechanistic route, summarised in Scheme III.14 one would expect the formation of

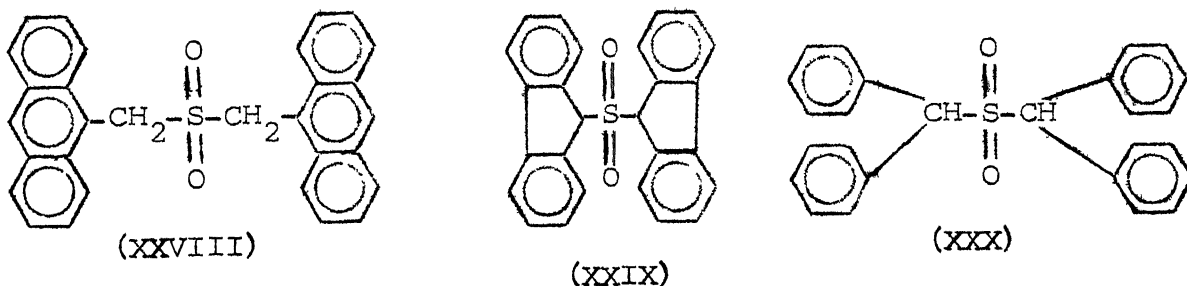
SCHEME III.14



a sulfonate anion along with the sulfinate anion¹⁷ in the reactions of all the four benzylic halides. The sulfinate anion in turn would readily react with the starting halide to yield a sulfone²⁷ (Eq. 17):



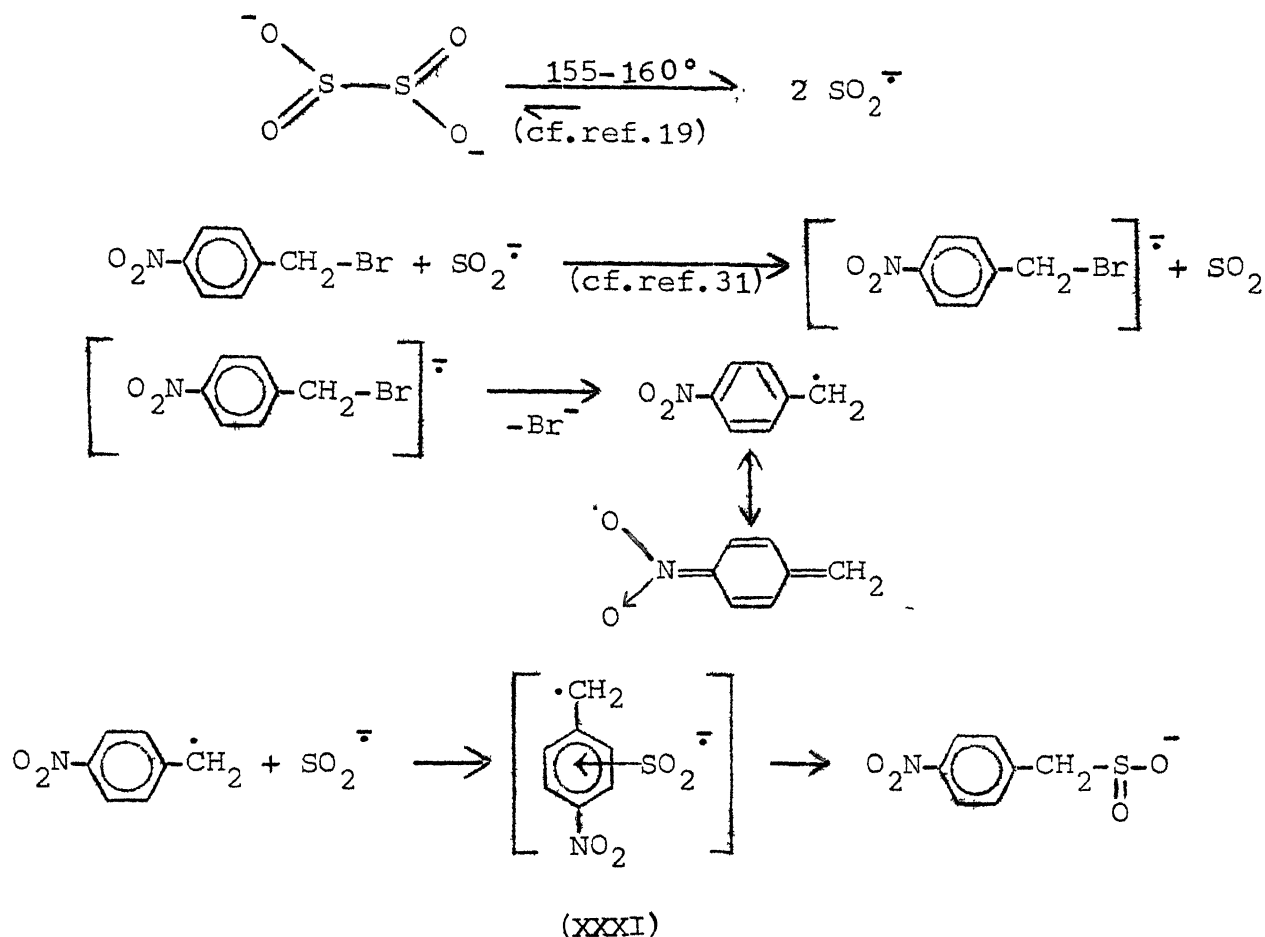
Although, the sulfone (XXVIII) expected to form in the reaction of 9-chloromethylantracene appears to be unknown in



the literature, the sulfones (XXXIX)²⁸ and (XXX)²⁹ expected in the reactions of 9-bromofluorene and benzhydryl chloride, respectively are stable compounds under our reaction conditions as the sulfone (XXV) obtained by us in the reaction of 4-nitrobenzyl bromide proved to be.³⁰ The fact that no sulfonic acids are obtained in any of the reactions and also that the sulfones (XXVIII), (XXIX) and (XXX) are not formed in the respective reactions indicates that the nucleophilic attack route (Scheme III.14) is not applicable to the reactions under study. This view is further supported by the fact that the undissociated dithionite anion is incapable of existence under our reaction conditions owing to its fragmentation¹⁹ into sulfur dioxide radical-anions. Indeed, the dithionite anion even when available for reaction is found to be too weak a nucleophile for direct S_N2 attack.²² It is obvious that sulfinatate anions are not important in the reactions of 9-bromofluorene, benzhydryl chloride and 9-chloromethylanthracene. Clearly, the sulfinatate anion intermediate necessary for the formation of the sulfone (XXV) in the reaction of 4-nitrobenzyl bromide must have been produced by an alternative path which is not available in the reactions of the other three benzylic halides. We suggest that the electron transfer-radical combination route outlined in Scheme III.15 satisfactorily accounts for the formation of the sulfinatate anion (leading to sulfone-XXV).

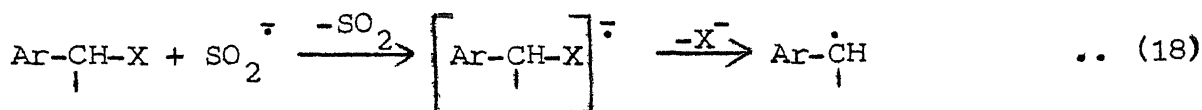
As the dithionite anion exists in equilibrium with the sulfur dioxide radical-anion ($\text{SO}_2^{\cdot-}$) even at room temperature,¹⁹

SCHEME III.15

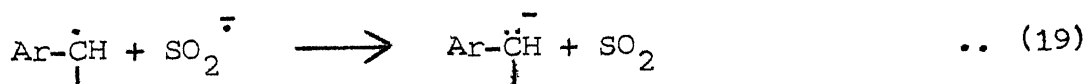


it is most likely that under elevated temperature conditions employed by us, the reagent largely exists as SO_2^- . This radical-anion reduces 4-nitrobenzyl bromide generating SO_2 gas and 4-nitrobenzyl radicals. These resonance stabilized radicals carrying an electron attracting nitro group associate with the electron rich sulfur dioxide radical-anions through π -interaction (see formulation -XXXI) giving ultimately, the 4-nitrobenzylsulfinate anion. The π -complex formation with electron deficient pyridinium compounds has been suggested earlier also

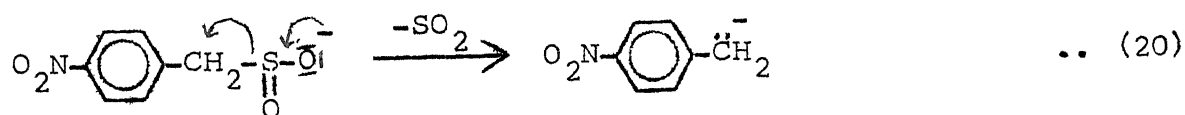
by Kosower and Bauer³² during their studies on dithionite reductions. Owing to the absence of an electron withdrawing group in the 9-fluorenyl, benzhydryl and 9-anthrylmethyl radicals produced from the corresponding halides as shown in Eq. (18),



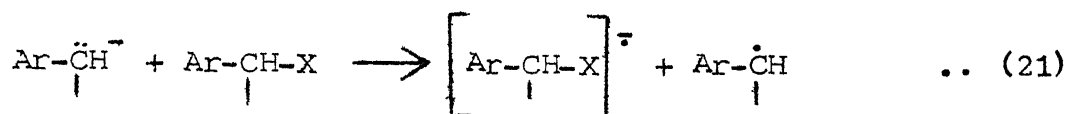
the π -interaction of the type discussed above does not take place in these cases. Consequently, the sulfinates which could have yielded sulfones in these reactions are not formed. In this situation, the available sulfur dioxide radical-anions (left after reaction of Eq. 18) may reduce a part of the radicals to the corresponding carbanions³³ (Eq. 19).



While 4-nitrobenzyl, 9-fluorenyl and 9-anthrylmethyl radicals are known to get readily reduced to carbanions by single electron transfer process, benzhydryl radical does not accept an electron³³ presumably due to the instability of the incipient benzhydryl carbanion. In the present study, the 4-nitrobenzyl carbanions might also arise from the decomposition of a portion of the corresponding sulfinate anion (Eq. 20):

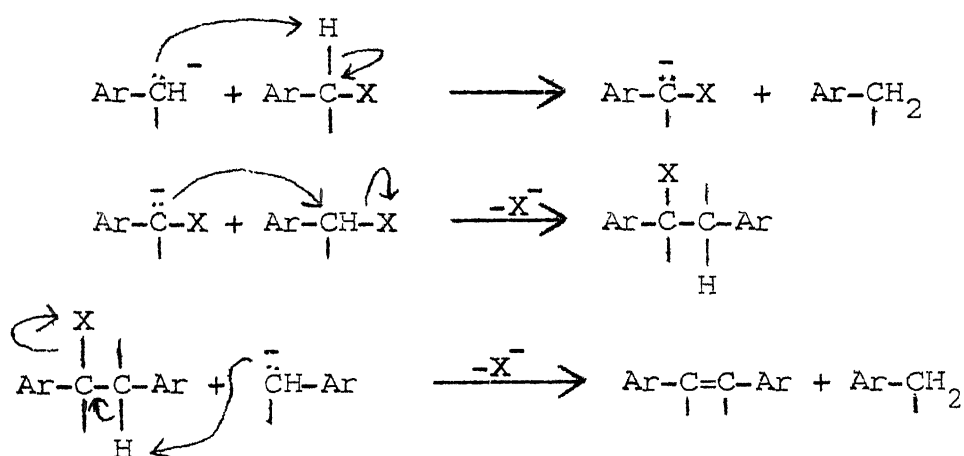


The benzylic carbanions viz., 4-nitrobenzyl, 9-fluorenyl and 9-anthrylmethyl carbanions obtained in the manner described above mainly get oxidized³⁴ to the radicals in presence of electron acceptors such as benzylic halides (Eq. 21); but



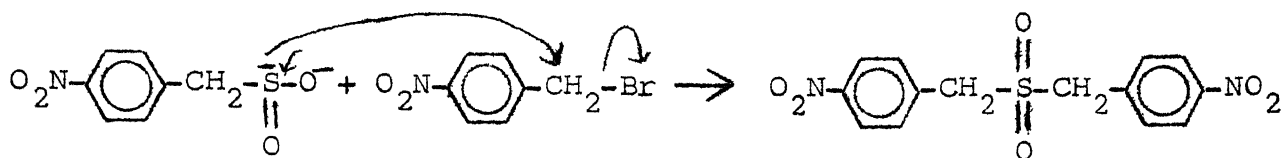
occasionally abstract protons from the benzyl positions of the starting halides ultimately giving the corresponding dehalogenation products i.e. (XXI), (XXII) and (XXIII) along with the olefinic dimers - (XXIV), (XXVI) and (XXVII), respectively as shown in Scheme III.16:

SCHEME III.16



Our results on the reactions of 4-nitrobenzyl bromide and 9-bromofluorene each with two different molar concentrations of the dithionite anion also support the above view point. Thus, the reactions (2) and (4) carried out with lower concentrations of the reducing agent compared to reactions (1) and (3),

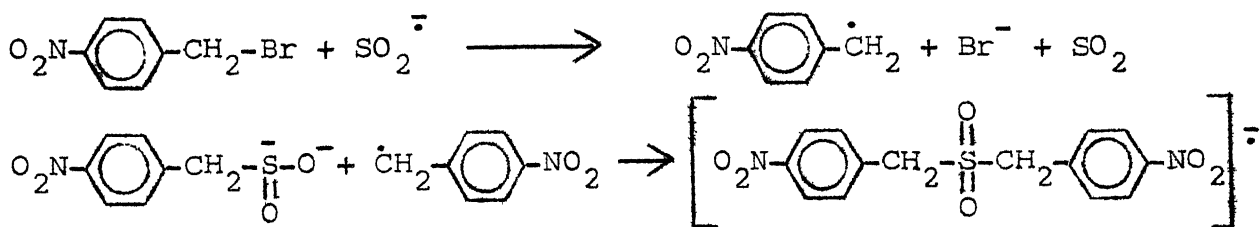
SCHEME III.17



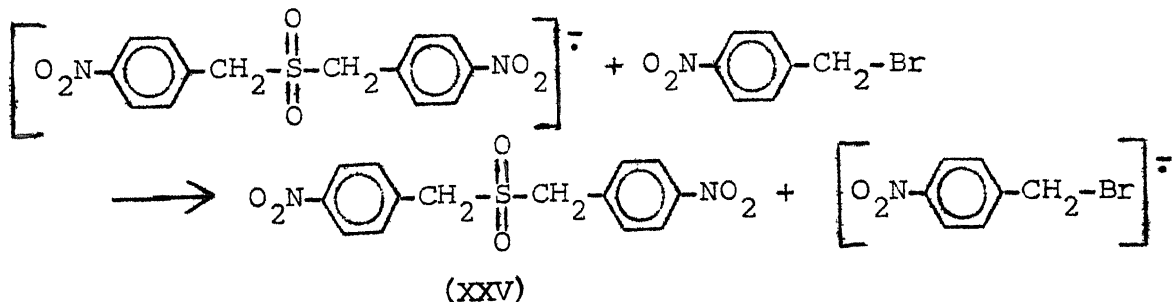
It should be noted in this connection that the reaction (1) of Table III.1 employing an excess of the reducing agent (i.e., $\text{SO}_2^{\cdot -}$) depletes the concentration of the starting halide faster as compared to the same process in reaction (2) of Table III.1. A nucleophilic displacement process (as of Scheme III.17) requiring the use of the initial halide would give sulfone (XXV) in lower yield in reaction (1) than in reaction (2). But, in actual practice reverse is found to be true. Hence the nucleophilic displacement process is ruled out of consideration.

An attractive pathway for sulfone formation, which in our opinion explains all the observations is the electron transfer free radical process outlined in Scheme III.18.

SCHEME III.18



(from Scheme III.15)



Coupling of the sulfinate anions with carbon radicals to form the corresponding sulphone radical-anions has been previously described by Kornblum and his coworkers.³⁷ The process of Scheme III.18 would continue giving sulfone (XXV) as long as the sulfinate anion and 4-nitrobenzyl radicals are present and at the same time, the extra electron from the sulfone radical-anion is accepted by an electron acceptor. In the absence of 4-nitrobenzyl bromide, the solvent would accept the extra electron.

III.4 Experimental

All the melting points were recorded using a MEL-TEMP melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer models-137 and 580 spectrophotometers. Known compounds were characterised by comparison of their IR spectra and TLC with those of authentic samples, the technique of mixed melting point, and by elemental analysis. Literature melting points are taken from the "Hand book of Chemistry and Physics" , 50th edition, R.C. Weast (Ed.) published by the Chemical Rubber Company, Cleaveland, Ohio, unless otherwise specified. Column chromatography was done over activated silica-gel (100-200 M). Silica-gel (asc-India) was used for TLC analyses.

Starting Materials

Dimethylformamide (SDS) was used in all the reactions after drying as described below. Sodium dithionite (Thomas Baker & Co.) was used. Silica-gel (Acme's) of 100-200 Mesh size was used for Column chromatography. 4-Nitrobenzyl bromide,³⁸ 9-bromofluorene,³⁹ benzhydryl chloride⁴⁰ and 9-chloromethyl-anthracene⁴¹ were prepared by known procedures.

Preparation of Deaerated, dry N,N-Dimethylformamide

Dimethylformamide was kept over calcium chloride for twenty four hours after which it was decanted into a one litre RB flask. It was distilled at atmospheric pressure and the fraction distilling over a temperature range of 152-154°C was collected. DMF was deaerated by passing pure and dry nitrogen continuously for half an hour into the solvent contained in a one litre RB flask mounted over magnetic stirrer base.

General Method for the Reduction of Benzylic Halides

In a 100 ml three-necked round-bottomed flask, mounted over a magnetic stirring base fitted with a device to pass pure, dry nitrogen, connected to a condenser and a mercury trap, was kept the organic halide (0.01 mol) mixed with sodium dithionite (0.015 mol or 0.005 mol) in a total of 50 ml of dry DMF. The flask was flushed with dry nitrogen for 10 min. Afterwards, the contents were heated over a temperature range of 155-160°C in a pre-heated oil-bath. The heating was continued for 1 hr. after which the oil-bath was removed and the flask cooled to

room temperature. The reaction mixture was worked up after adding to acidified water. The products were extracted with solvent ether, the extract washed with an excess of water, dried over MgSO_4 (anhydrous) and concentrated to give a crude mixture which was charged on a column of activated silica-gel (100-200 M). The products were separated by eluting the column with petroleum ether (b.p. 60-66°), petroleum ether (b.p. 60-66°)-benzene and benzene as eluants. These were characterised by comparison of their IR spectra with those of authentic samples, mixed melting points and TLC.

Reaction of 4-Nitrobenzyl bromide with Sodium Dithionite

(a) Halide to dithionite molar ratio-1:1.5

In a 100 ml three-necked RB flask mounted over a magnetic stirring base was placed 4-nitrobenzyl bromide (2.16 g, 0.01 mol), sodium dithionite (2.88 g, 0.015 mol) and 50 ml of dry DMF. The contents of the flask were flushed with dry nitrogen for 10 min. and then heated at 155-160° for one hour in a pre-heated oil-bath. The reaction started with evolution of sulfur dioxide which was tested by passing the gas into a 2% aqueous solution of potassium dichromate. The gas evolution was fast during the first 5 min., but slow evolution of SO_2 continued upto a period of ca. 35 min. At the end of one hour, the oil-bath was removed and the reaction mixture cooled to room temperature. It was worked up by adding it to acidified water and extracting with solvent ether. The combined ethereal extract was washed

with an excess of water, dried over MgSO_4 (anhydrous) and concentrated to give a product mixture which was charged on a silica-gel column. Elution of the column with petroleum ether (b.p. 60-66°), petroleum ether (b.p. 60-66°):benzene (75:25), petroleum ether (b.p. 60-66°):benzene (50:50), benzene and methanol gave 4-nitrotoluene, m.p. 51°, lit. 52°C (0.19 g, ~14%), 4,4'-dinitrobibenzyl, m.p. 178°, lit. 178-179°C (0.34 g, ~25 %), 4,4'-dinitrostilbene, m.p. 290-291°, lit. 291-293°C (0.080 g, ~6%) and di(4-nitrobenzyl)sulfone, m.p. 258°, lit. 260°C³⁰ (0.873 g, ~52%). Compounds were identified by comparison of IR spectra with those of authentic samples, by mixed m.p. technique, TLC and C, H and N analyses.

In a separate experiment, GLC analysis of the reaction mixture using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of 4-nitrobenzaldehyde and 4-nitrobenzyl alcohol each in 2% yield (estimated by the calibration method) as the additional products.

(b) Halide to dithionite molar ratio - 1:0.5

The above reaction was repeated using 4-nitrobenzyl bromide (2.16 g, 0.01 mol), sodium dithionite (0.96 g, 0.005 mol) and 50 ml of dry DMF under otherwise similar conditions. The reaction was worked up as usual after cooling to room temperature and the products extracted with ether. Chromatography of the product mixture on silica-gel column using petroleum ether (b.p. 60-66°), petroleum ether (b.p. 60-66°):benzene (75:25),

petroleum ether (b.p. 60-66°):benzene (50:50), benzene and methanol gave 4-nitrotoluene (0.096 g, ~7%), 4,4'-dinitrobenzyl (0.448 g, ~33%), 4,4'-dinitrostilbene (0.040 g, ~3%) and di-(4-nitrobenzyl)sulfone (0.722 g, ~43%). Compounds were identified by comparison of their IR spectra, mixed m.p. technique, TLC and C, H and N analyses.

In a separate experiment, GLC analysis of the reaction mixture using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of 4-nitrobenzaldehyde and 4-nitrobenzylalcohol in 2% and 3% yields, respectively (estimated by the calibration method) as the additional products.

Reaction of 4-Nitrobenzyl bromide with DMF

The above reaction was repeated using 4-nitrobenzyl bromide (2.16 g, 0.01 mol) and 50 ml of dry DMF without the reducing reagent (sodium dithionite) under otherwise identical conditions. GLC analysis of the reaction mixture using 10% SE-30 on Crom-P (85-100 m) column of 2 m length indicated the presence of 4-nitrobenzaldehyde (0.135 g, ~9%) and 4-nitrobenzylalcohol (0.29 g, ~19%) by calibration method.

Reaction of 9-Bromofluorene with Sodium Dithionite

(a) Halide to dithionite molar ratio - 1:1.5

In a three-necked 100 ml RB flask mounted over a magnetic stirring base was placed 0.01 mol (2.45 g) of 9-bromofluorene and sodium dithionite (2.88 g, 0.015 mol). Dry DMF (50 ml) was

added to the flask and the system flushed with pure and dry nitrogen. The contents of the flask were heated over a temperature range of 155-160°C for one hour in a pre-heated oil-bath. The reaction started with the evolution of sulfur dioxide which was tested by passing the gas into a 2% solution of potassium dichromate. No evolution of sulfur dioxide was observed after ten minutes. After one hour period the contents of the flask were cooled to room temperature and the reaction mixture added to a beaker containing acidified water. The products were extracted with solvent ether, extract washed with water and dried over anhydrous MgSO_4 . The product mixture collected after removing the solvent showed three spots on TLC corresponding to fluorene, bifluorenylidene and 9,9'-bifluorenyl. The crude mixture of products was charged on an activated silica-gel column. Elution of the column using petroleum ether (b.p. 60-66°) and petroleum ether (b.p. 60-66°):benzene (50:50) gave fluorene, m.p. 116°, lit. 116-7° (0.20 g, ~12%), bifluorenylidene, m.p. 193-195°, lit. 194-5° (0.098 g, ~6%), 9,9'-bifluorenyl, m.p. 245-247°, lit. 247° (1.20 g, ~73%), fluorenone (0.035 g, ~2%) and 9-fluorenol (0.055 g, ~3%). Compounds were identified by comparison of IR spectra with those of authentic samples, mixed m.p. technique, TLC and C, H analyses.

(b) Halide to dithionite molar ratio - 1:0.5

The above reaction was repeated using 0.01 mol (2.45 g) of 9-bromofluorene and 0.005 mol (0.96 g) of sodium dithionite in

50 ml of dry DMF. The reaction was allowed to proceed for one hour over a temperature range of 155-160°. The reaction mixture was poured into acidified water. The products were extracted with solvent ether, the extract washed with water and dried over MgSO_4 (anh.). Separation of products on a silica-gel column as described in the above reaction gave fluorene (0.133 g, ~8%), bifluorenylidene (0.050 g, ~3%), 9,9'-bifluorenyl (1.32 g, ~80%), fluorenone (0.035 g, ~2%) and 9-fluorenol (0.051 g, ~3%). The products were characterised as described in the previous experiment.

Reaction of 9-Bromofluorene with DMF

9-Bromofluorene (2.45 g, 0.01 mol) and 50 ml of dry DMF were heated in an oil-bath over a temperature range of 155-160° under an atmosphere of N_2 for one hour. The reaction mixture after work up in the usual manner gave fluorenone (0.19 g, ~11%) and 9-fluorenol (0.31 g, ~17%) on an activated silica-gel column using petroleum ether (b.p. 60-66°)-benzene (50:50) and benzene as eluants.

Reaction of Benzhydryl Chloride with Sodium Dithionite

In a 100 ml three-necked RB flask mounted over a magnetic stirring base, fitted with a gas passing adapter, a condenser and a mercury trap was placed benzhydryl chloride (2.02 g, 0.01 mol), sodium dithionite (2.88 g, 0.015 mol) and dry DMF (50 ml). The reaction mixture was heated over a temperature

range of 155-160° for an hour as in the previous experiments. The reaction started with the evolution of sulfur dioxide which was tested by passing the gas into a 2 % solution of potassium dichromate. No evolution of sulfur dioxide was observed after ten minutes. After the one hour period of heating, the contents of the flask were cooled to room temperature. The reaction mixture was added to acidified water, the products extracted with ether, the extract thoroughly washed with water and dried over MgSO_4 (anhyd.). On concentration of the ethereal extract a solid (0.72 g) melting at 212°C crystallised out. This solid was identified as 1,1,2,2-tetraphenylethane, lit. m.p. 212-213°C. Complete removal of the solvent from the mother liquor gave a crude mixture of products which on chromatography over activated silica-gel column using petroleum ether (b.p. 60-66°) and petroleum ether (b.p. 60-66°) : Benzene (75:25) as eluants gave fluorene (0.050 g, ~3%) and an additional amount of 1,1,2,2-tetraphenylethane (0.627 g). The total yield of 1,1,2,2-tetraphenylethane thus obtained was 81%. The compounds were characterised by comparison of their IR spectra with those of the authentic samples, TLC, mixed melting point technique and C, H analysis.

In a separate experiment, GLC analysis of the reaction mixture using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of benzhydrol and benzophenone each in 2% yield (estimated by the calibration method) as additional products.

Reaction of Benzhydryl Chloride with DMF

The above reaction was repeated with benzhydryl chloride (2.02 g, 0.01 mol) and 50 ml of dry DMF in the absence of the reducing agent (sodium dithionite) under otherwise similar conditions. GLC analysis of the reaction mixture using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of benzophenone (0.125 g, ~7%) and benzhydrol (0.295 g, ~16%) by calibration method.

Reaction of 9-Chloromethylantracene with Sodium Dithionite

The reaction between sodium dithionite (2.88 g, 0.015 mol) and 9-chloromethylantracene (2.265 g, 0.01 mol) in dry DMF (50 ml) was conducted in the same manner as the earlier experiments. The reaction started with evolution of SO_2 gas (tested by passing into a 2% solution of potassium dichromate) which continued for a period of 10 min. The reaction was worked up after adding the cooled reaction mixture to acidified water. A yellow precipitate which appeared on pouring the reaction mixture into water was filtered off, washed with ether and identified as 1,2-di-(9-anthryl)-ethane (m.p. 309-310°, lit.⁴² 312°C). The filtrate was extracted with ether, the ethereal extract was washed with water and dried (MgSO_4). The solvent was removed to give a crude mixture of products which on tlc analysis showed spots corresponding to 9-methylantracene, 1,2-di-(9-anthryl)-ethane, 1,2-di-(9-anthryl)-ethylene, 9-formyl-anthracene and 9-hydroxylmethylantracene. The crude mixture

of products was shaken well with hexane when a part of it remained as insoluble solid which was filtered. The hexane insoluble portion was identified as 1,2-di-(9-anthryl)-ethane. Total yield of 1,2-di-(9-anthryl)-ethane was 1.49 g (~78%). Column chromatography of the hexane soluble portion on silica-gel (100-200 M) using petroleum ether (b.p. 60-66°) gave 9-methylanthracene (0.095 g, ~5%; m.p. 80°, lit. 81.5°C). A tarry material at the top of the column, presumably containing 1,2-di-(9-anthryl)ethylene, 9-formylanthracene and 9-hydroxymethylanthracene, could not be separated. Both the compounds were characterized by mixed melting point technique and comparison of their IR spectra with those of the authentic samples.

Reaction of 9-Chloromethylanthracene with DMF

The above reaction was repeated using 9-chloromethylanthracene (2.26 g, 0.01 mol) and DMF (50 ml) in the absence of sodium dithionite under otherwise identical conditions. After work up in the manner detailed above, tlc of the crude mixture showed spots corresponding to 9-formylanthracene and 9-hydroxymethylanthracene. A qualitative comparison on tlc of the this product mixture and that obtained in the previous experiment indicated the presence of larger amounts of 9-formylanthracene and 9-hydroxymethylanthracene in the blank experiment.

III.5 References

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CHAPTER IV

REDUCTION AND DIMETHYLAMINATION OF BENZYLIC HALIDES IN PRESENCE OF Co(II) AND Fe(II) IN DMF MEDIUM

IV.1 Abstract

Reactions of benzyl chloride, 4-nitrobenzyl bromide, 9-bromofluorene, benzhydryl chloride and trityl chloride with Co(II) chloride or Fe(II) oxalate in DMF at 155-60° were studied under carefully varied reaction conditions. Based on the product analysis, blank experiments in the absence of metal ions and other control experiments, it is concluded that under the conditions employed, DMF brings about nucleophilic displacement of halogen by S_N2 type attack on 4-nitrobenzyl bromide and S_N1 type attack on all other halides, through its oxygen atom. Dimethylamination takes place when DMF is oxidized by electron transfer process into the DMF radical-cation which couples with benzylic radicals easily. Cobalt(II) influences the course of all the reactions by acting as electron donor to the halide via outer sphere electron transfer process. Iron(II) behaves similarly with 4-nitrobenzyl bromide; but preferentially forms an

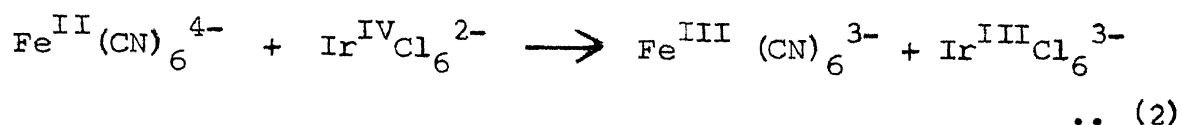
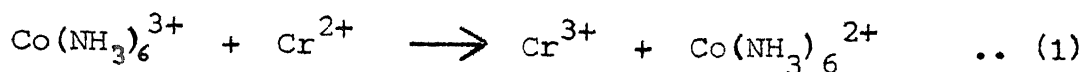
organoiron complex with other halides via oxidative addition involving a 3-center, concerted, frontside nucleophilic displacement mechanism. The unstable organoiron complex produces dimeric products by a facile, concerted orbital symmetry allowed process. Radical intermediates are not present in the latter reactions. The mechanistic conclusions made here are tentative and many more data are needed for making conclusive assertions.

IV.2 Introduction

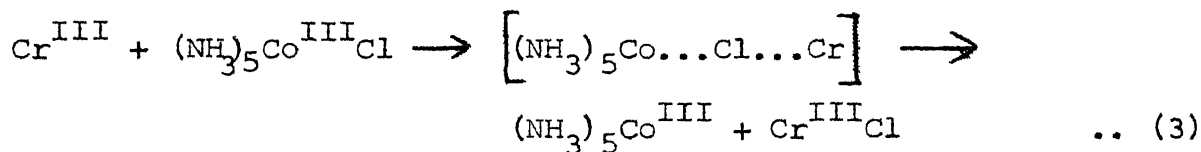
Metal ions and metal complexes are finding increasing use in organic chemistry both as reagents and as catalysts for a variety of synthetic transformations. Metal catalysis is important in industrial chemistry since it allows for high selectivity and economic efficiency. In order to enrich this important field of metal catalysis, in organic chemistry, a mechanistic understanding of the chemical interactions between the metal and various organic substrates is desirable. Although organometallic compounds are known to play key roles as reactive intermediates in a number of these systems, surprisingly little is precisely known about how these organometallic intermediates are formed and how do they undergo further transformations. Most of the reactions in question are believed to proceed by redox processes.

Oxidation-reduction reactions involving metal ions and their complexes are mainly of two types:¹⁻⁷ inner-sphere

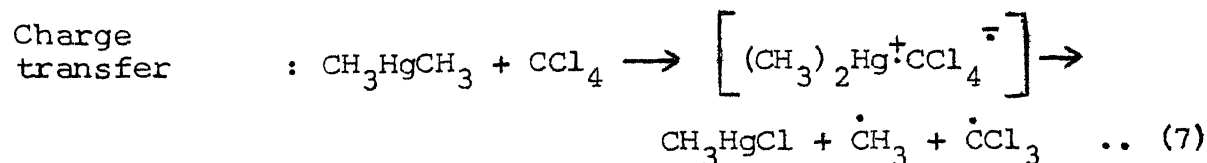
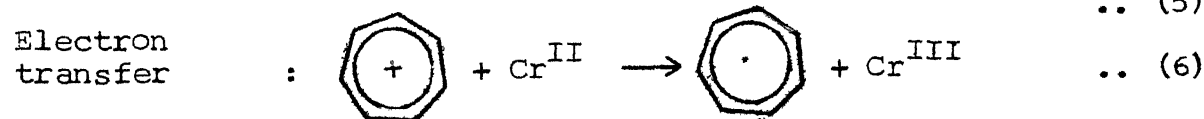
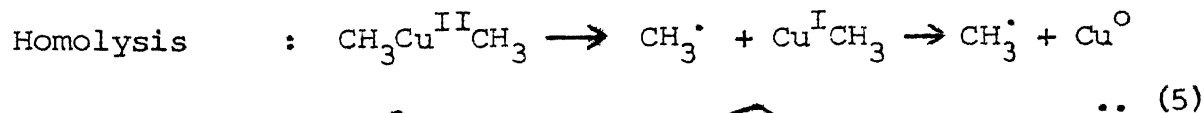
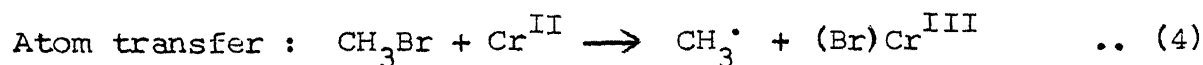
(ligand transfer) and outer-sphere (electron transfer) reactions. During electron transfer reactions, the coordination spheres of the metal ions remain intact. Such electron transfer processes can be visualized as electron "tunnelling" through a potential barrier between regions of lowest energy as represented in Eqs. (1) and (2):



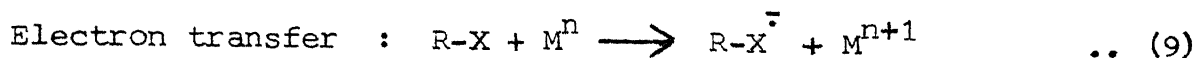
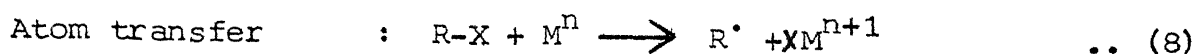
By contrast, ligand transfer reactions are believed to proceed via a bridged activated complex in which the two metal ions are connected by a common bridging ligand as shown by an example in Eq. (3):



Metal ions or uncharged metal complexes may be used to produce radicals by various processes shown in Eqs. (4)-(7):⁸⁻¹²



The reduction of organic halides by metal ions or metal complexes may be formally represented by three different pathways outlined below:

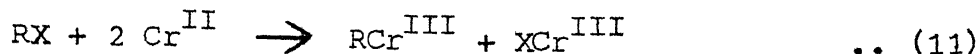


Whereas the first two mechanisms involve radical intermediates, the third occurs without the intervention of paramagnetic species. In practice, these mechanisms are difficult to distinguish experimentally from each other, since they differ mainly in the timing of the bond formation and bond rupture sequence. In the atom transfer process, radicals are produced via a complex (an intermediate and/or a transition state) in which the halogen constitutes the bridging ligand forming part of the coordination sphere of the metal reductant, e.g. (R-X-M). In the electron transfer process, the coordination shell of the reductant is not penetrated (as mentioned previously), and the carbon-halogen bond remains intact in the transition state. Carbon radicals are formed subsequently by fragmentation of the radical-anion of the organic halide.

Thus, atom transfer and electron transfer processes are oxidation-reduction reactions proceeding via inner-sphere and outer-sphere mechanisms, respectively. These two processes can

be distinguished if the products are substitution stable.

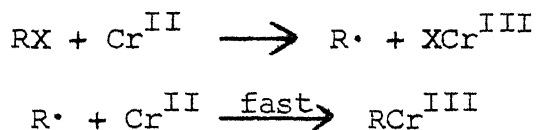
The reduction of alkyl halides by Cr(II),¹³ for example, is kinetically first order in each reactant (Eq. 11):



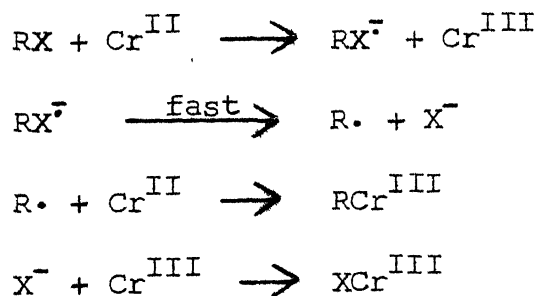
The products are substitution stable and the available evidence suggests the occurrence of 'atom transfer' process^{14,15} in the cases under reference. Thus, one may consider the action of the substitution-labile species Cr(II) on an organic halide by two distinct pathways outlined in Scheme IV.1.

SCHEME IV.1

Path I: Atom transfer process



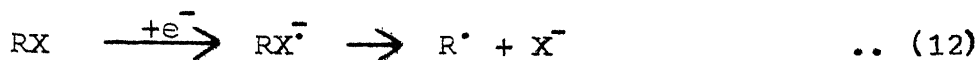
Path II: Electron transfer process



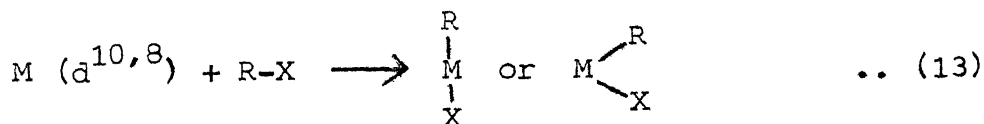
Both products RCr(III) and XCr(III) are substitution-stable as is Cr(III) which is not converted by halide ion to XCr(III) under the reaction conditions.^{14,15} As the last step of Path II would not be fast enough to produce XCr(III), it is concluded

that the halogen must have been transferred during the reduction shown in the first step of Path I.

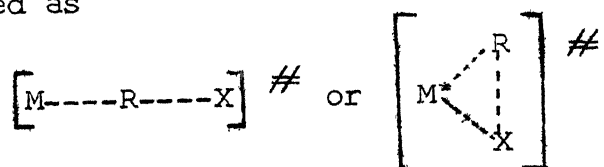
Electron transfer reduction of organic halides has been affected by such powerful reagents as alkali naphthalenes, lithium benzophenone ketyl and dicarbanions, etc.¹⁶⁻²⁰ to give radical anions which cleave to produce radicals.



Oxidative addition represents a ubiquitous class of reactions in which the oxidation of a metal complex by an electrophile is accompanied by a concomitant increase in its coordination number²¹⁻²³ (Eq. 13):



This process may proceed through either (i) concerted two-equivalent transformations, or (ii) successions of one-equivalent changes involving radicals. The former may involve nucleophilic displacement of halide by attack of the metal at the carbon centre, including either a 2- or 3-centre transition state represented as

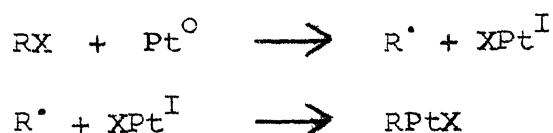


respectively. The 2-centre transition state must result in the stereochemical inversion of configuration at the carbon centre,

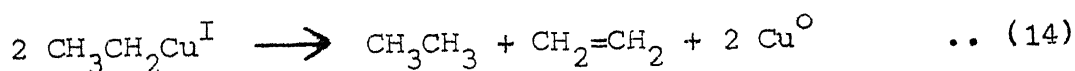
while the 3-centre transition state would lead to retention of configuration at carbon.

The process outlined in Scheme IV.2 involves successive one-equivalent changes, with radicals as intermediates.^{24,25}

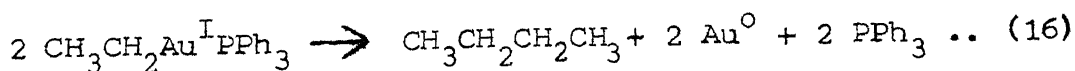
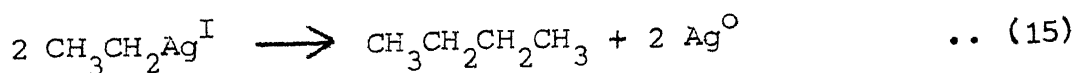
SCHEME IV.2



Free radicals are usually not the prime intermediates in the decomposition of most of the organometals and molecular processes are involved in disproportionation and combination of alkyl groups. This is evident from the selective decomposition of certain organometals to produce only disproportionation products^{26,27} (Eq. 14):

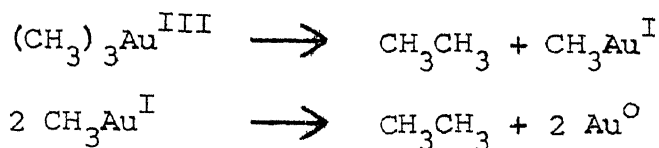


whereas others afford only coupling products²⁸⁻³⁰ (Eqs. 15 & 16):



Organometals can also undergo homolytic fission to give alkyl radicals and organometal radicals. Alkyl radicals can subsequently undergo bimolecular reactions to afford coupling products or undergo disproportionation.

The reductive coupling of alkylmetals resulting in C-C bond formation can proceed either intermolecularly from RM or intramolecularly from R_2M . The examples of intermolecular reactions are shown in Eqs. (15) and (16). Reductive coupling of two alkyl groups attached to a single metal occurs in organo-gold(III), -cobalt(III), -nickel(II), and platinum(II,IV) derivatives. For example, trimethyl gold(III) spontaneously undergoes reductive coupling at -40°C to afford metallic gold and ethane:³¹

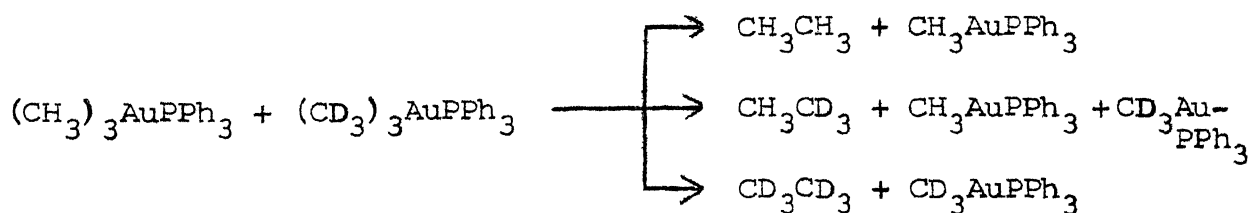


The decomposition of more stable phosphine adducts, $(\text{CH}_3)_3\text{-AuL}$, where L = phosphines³² at 80°C gave ethane and CH_3AuL (Eq. 17):



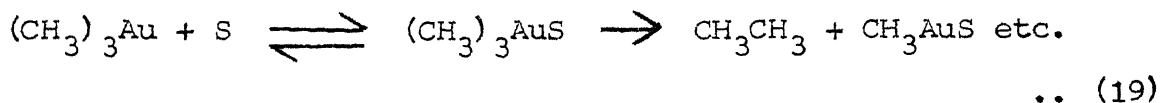
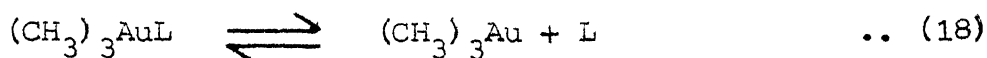
The product CH_3AuL itself undergoes further decomposition to ethane and a gold mirror.

Solutions of an equimolar mixture of $(\text{CH}_3)_3\text{AuPPh}_3$ and $(\text{CD}_3)_3\text{AuPPh}_3$ gave substantial amounts of cross-over product (CH_3CD_3) when decompositions were carried out in decalin, chlorobenzene or ethereal solvents.³⁴ In polar solvents such as



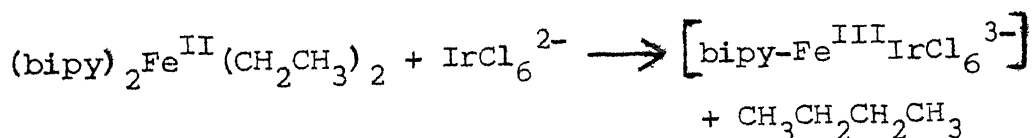
dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), the decomposition afforded CH_3CH_3 and CD_3CD_3 , with only trace amounts of CH_3CD_3 .

The intermediate, $(\text{CH}_3)_3\text{Au}$, can be effectively intercepted by better coordination solvents such as DMSO and DMF (Eq. 19)



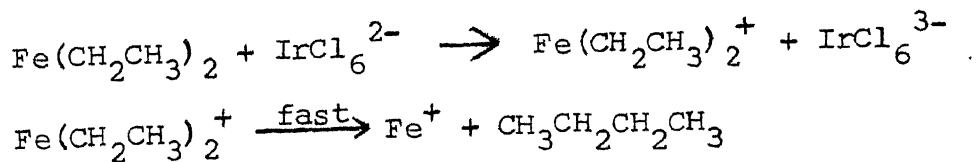
to afford labile complexes from which reductive elimination occurs by an intramolecular pathway without scrambling the methyl groups in the product.

When dialkyliron(II) derivatives are treated at room temperature with a variety of one-equivalent oxidants, including IrCl_6^{2-} , Ce(IV) and Cu(II) , the spontaneous coupling of alkyl groups takes place in high yields, with little or no disproportionation,³³ e.g.,



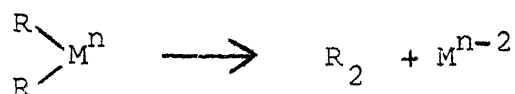
Here, conversion to the metastable paramagnetic dialkyliron(III) intermediate followed by rapid coupling is indicated (Scheme IV.3):

SCHEME IV.3

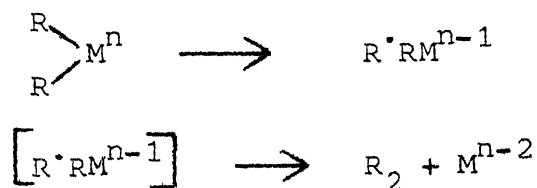


where $\text{Fe} = \text{Fe}^{\text{II}}(\text{bipy})_2$

Reductive coupling of two alkyl ligands attached to a single metal centre can also take place by an orbital symmetry allowed process:³⁴



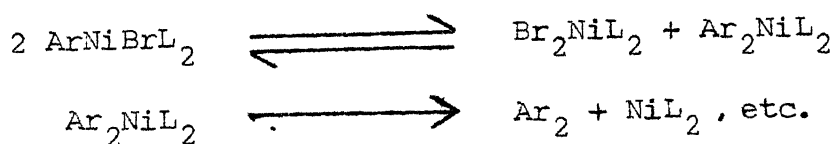
where n represents the formal oxidation state. Such a process, however, is difficult to distinguish from a stepwise, homolytic process,



particularly if it occurs within a solvent cage. CIDNP studies of the thermal decomposition of dialkyl mercury(II) suggest that such cage reactions are possible.³⁵

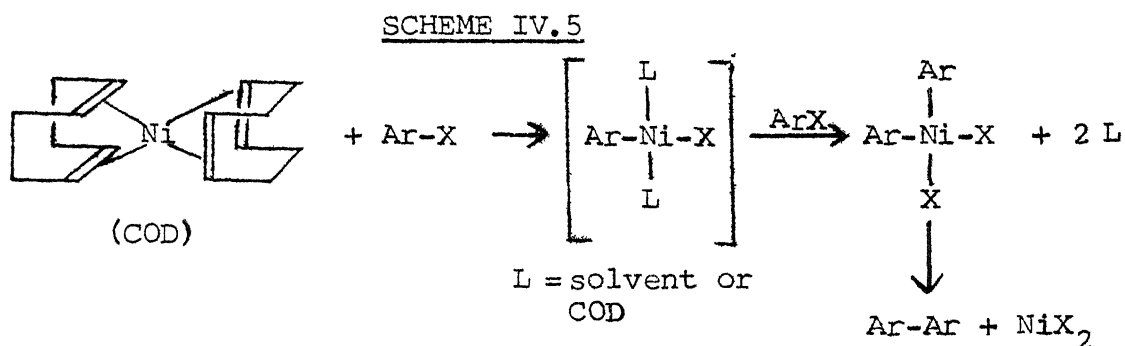
The thermal decomposition of aryl- and benzyl-nickel(II) derivatives, $\text{PhNi}(\text{Br})(\text{PPh}_3)_2$ and $\text{PhCH}_2\text{Ni}(\text{Br})(\text{PPh}_3)_2$, affords coupled products Ph_2 and $\text{PhCH}_2\text{CH}_2\text{Ph}$, respectively, in quantitative yields.³⁶ The dimerization presumably occurs by the reductive coupling of Ar_2NiL_2 according to Scheme IV.4, without the intervention of radicals. Tetraphenyl tellurium yields diphenyl³⁷ on thermal decomposition.

SCHEME IV.4

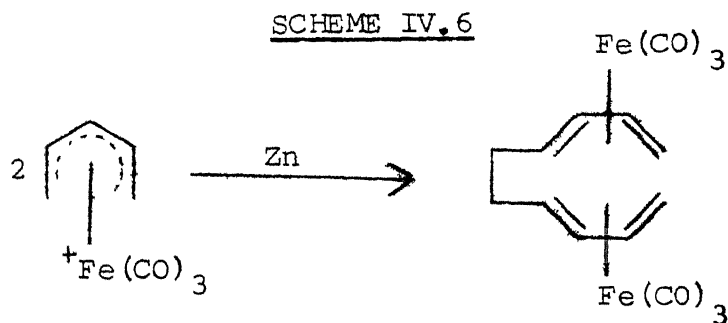


Reaction of aryl halides with bis-(1,5-cyclooctadiene)-nickel(0) (COD) results in the formation of diphenyls in DMF.³⁸

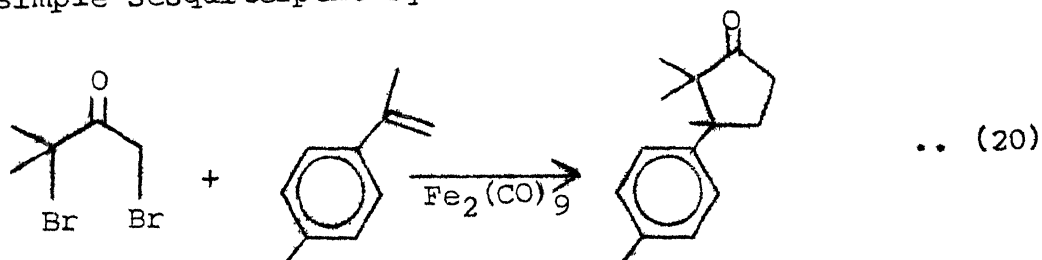
The mechanism proposed for this, is shown in Scheme IV.5:



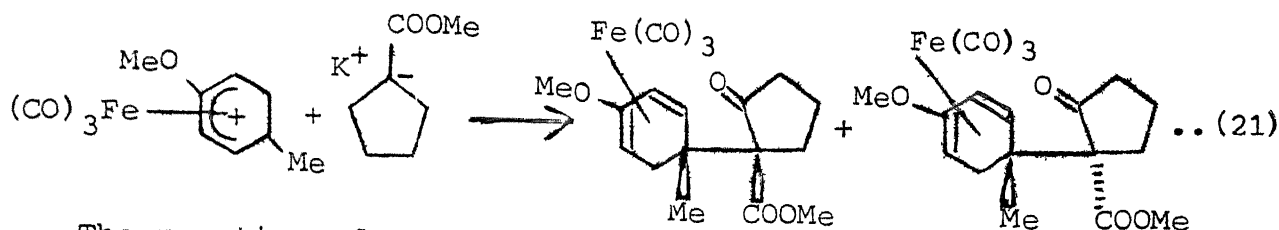
Reduction of dimagnetic organometals may also induce coupling. Thus, treatment of the cationic pentadienyliron complex, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$, with zinc results in the formation of a new C-C bond^{39,40} as shown in Scheme IV.6:



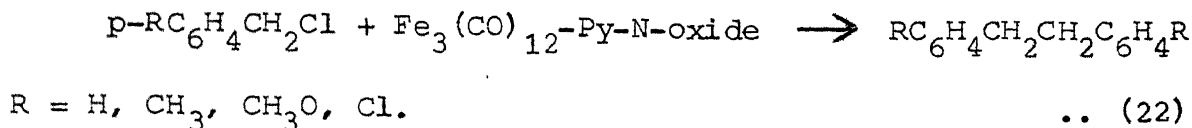
The iron carbonyl promoted cyclocoupling reaction between α, α' -dibromoketones and arylated olefins provides a new tool for the synthesis of 3-arylcyclopentanones.⁴¹ Equation (20) shows a simple sesquiterpene synthesis⁴² following the same method.



Iron carbonyl complexes have also been used in the synthesis of tricothecane⁴³ (Eq. 21):



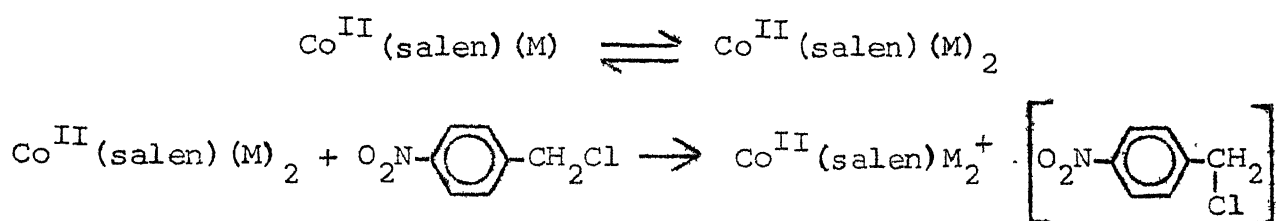
The reaction of p-substituted benzyl chlorides with $\text{Fe}_3(\text{CO})_{12}$ -pyridine-N-oxide reagent system afforded 1,2-diphenylethane derivatives⁴⁴ (Eq. 22):



The reaction presumably occurs by the thermal decomposition of an iron-carbonyl complex containing a benzyl group which is produced during the course of the reaction. An attempt to isolate the complex in pure state was unsuccessful because of its instability. Aromatic aldehydes also undergo reductive coupling to give the corresponding diols as major products⁴⁵ with the same reagent.

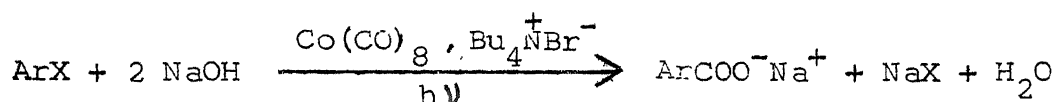
Iron(II) is known to transfer electrons to diazonium salts to give aryl radicals which have been trapped by 4-methyl-3-penten-2-one and isolated as azo compounds.⁴⁶

4-Nitrobenzyl bromides are reduced by N,N'-bis(salicylidene)-ethylenediamino-1-methylimidazole-cobalt(II) $[\text{Co}^{\text{II}}(\text{salen})\text{M}]$ by outer-sphere mechanism⁴⁷ according to Scheme IV.7:

SCHEME IV.7

Outer-sphere electron transfer is promoted by the nitro group which stabilizes the radical-anion.⁴⁸

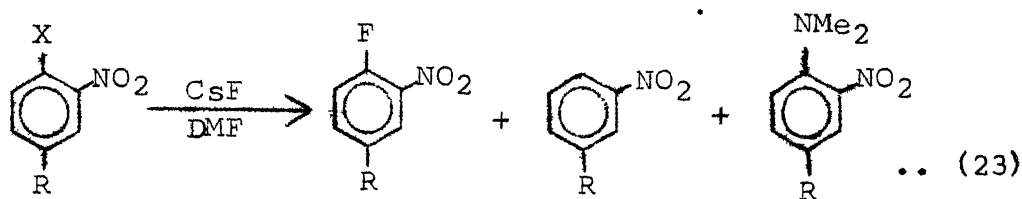
The phase transfer catalyzed, cobalt carbonyl catalyzed carbonylation of aryl and vinyl bromides under photostimulation affords the corresponding unsaturated acids in high yield.



These reactions are believed to be taking place by $\text{S}_{\text{RN}}1$ pathway.⁴⁹

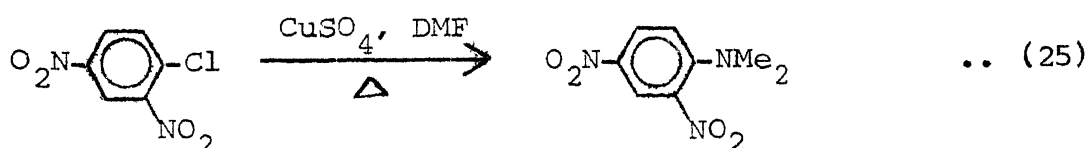
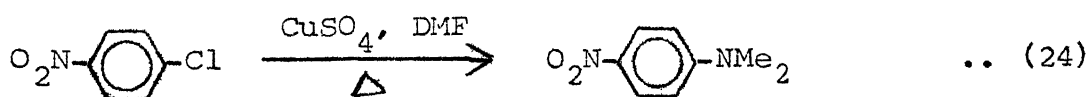
Aryl halides undergo dimerization with copper (Ullmann reaction)⁵⁰ possibly via two consecutive steps: (i) a nucleophilic reaction of copper with the aromatic halide to form an activated complex at the metal surface, (ii) the reaction of the activated complex with a second molecule of aromatic halide to form a biaryl plus copper halide.

Halonitroaromatic compounds are known to undergo dimethylamination reactions in DMF in the presence of catalysts like CsF ,⁵¹ CuSO_4 or CuCN ⁵² as shown in Eqs. (23)-(25):



R = NMe₂, OMe, Me, H, NO₂ etc., X = Cl, Br, I.

When X = Br and R = NO₂ the dimethylation product is obtained in quantitative yields.



In an attempt to rationalize many diversities in the reactions of metal ions with organic halides and to study the mechanistic process of catalysed dimethylation by DMF, we decided to examine a few reactions of benzylic halides with Co(II) and Fe(II) salts in DMF.

IV - 3 Results and Discussion

In the reduction of organic halides with metal ions or metal complexes, it is observed that variation in mechanistic pathways often occurs with a change in the metal reagent; but the mechanistic differences are due more to the structure of the organic halide than to the metal itself. It is clear,

however, that only minor differences in energetics are responsible for separating mechanisms⁵² and more extensive studies are required before any general mechanistic pattern can be developed from the properties of the metal reductant.

The present study aims at examining the behaviour of Fe(II) and Co(II) compounds with benzylic halides. Reactions of Fe(II) were carried out with benzyl chloride (I), 4-nitrobenzyl bromide (II), 9-bromofluorene (III), benzhydryl chloride (IV) and trityl chloride (V) in DMF at 155-60° under different experimental conditions. While both the primary halides (I) and (II) yielded several products listed in Table IV.1, the two secondary halides (III) and (IV) gave benzylic dimers, almost exclusively (Table IV.2). The tertiary halide viz., trityl-

Table IV.1. Reactions of Primary Benzylic Halides I and II (Ar-CH₂-X; 0.01 mol) with Fe(II) oxalate in DMF at 155-60° for 1 hr (I = benzyl chloride and II = 4-nitrobenzyl bromide)

Run	Halide	Molar ratio Halide: Fe(II)	R _x ⁿ Atmosphere	% yield of products				
				ArCH ₃	(Ar-CH ₂) ₂	ArCH ₂ OH	ArCHO	ArCH ₂ NMe ₂
1 ^{a,b}	I	1:1	N ₂	-	10	7	trace	2
2	II	1:1	N ₂	10	16	3	4	62
3	II	1:0.5	N ₂	5	7	12	6	48
4	II	1:1	O ₂	-	-	6	23	61
5 ^b	II	1:0	N ₂	-	-	8	4	23

a, Blank reaction in the absence of Fe(II), showed benzyl alcohol (8%) and traces of benzaldehyde and benzyl dimethylamine, but no bibenzyl among the products.

b, Starting halides remaining unreacted were 69% in run 1 and 57% in run 5.

Table IV.2. Reactions* of Secondary Benzylic Halides III and IV ($\text{Ar}_2\text{CH-X}$; 0.01 mol) with Fe(II) oxalate in DMF at 155-60° (III = 9-bromofluorene; IV = benzhydryl-chloride)

Run	Molar ratio Halide: Fe(II)	Time (hr)	Rx ⁿ Atmosphere	% Yield of the principal product ^c (9,9'-bifluorenyl) from Halide (III)	% Yield of the principal product ^d (1,1,2,2-tetraphenylethane) from Halide (IV)
6,7	1:2	1	N ₂	95	85
8 ^e , 9 ^f	1:1	1	N ₂	95	86
10,11	1:0.5	1	N ₂	85	83
12,13	1:0.25	1	N ₂	44	40
14,15	1:1	12	N ₂	90	86
16,17	1:1	1	O ₂	92	84
18,19	1:1 (cyclohexene 0.015 mol was added)	1	N ₂	94	83

* A preliminary analysis of the aliquots removed from the reaction mixtures of the repeat runs 8 and 9 respectively at intervals clearly showed the rapid disappearance of the benzylic halides and slower formation of the dimeric products in each case.

c, In all the experiments with 9-bromofluorene, (i.e., runs 6, 8, 10, 12, 14, 16 and 18), traces of bifluorenylidene and 9-fluorenol were detected among the products; but no fluorenone or 9-dimethylaminofluorene could be detected.

d, In all the experiments with benzhydryl chloride (i.e., runs 7, 9, 11, 13, 15, 17 and 19), benzhydrol was detected as a minor product; but no benzophenone or benzhydryldimethylamine could be detected.

e, Blank experiment of run 8 conducted with 9-bromofluorene in the absence of Fe(II) indicated the presence of 9-fluorenol (17%) fluorenone (11%) and 9-dimethylaminofluorene (14%) as detectable products, besides unreacted starting halide.

f, Blank experiment of run 9 conducted with benzhydryl chloride in the absence of Fe(II), indicated the presence of benzhydrol (16%), benzophenone (7%) and benzhydryldimethylamine (6%), besides unreacted starting halide.

chloride (V), however, yielded triphenylcarbinol as the major product accompanied by a minor component of triphenylmethane (Table IV.3).

Table IV.3. Reaction of Trityl chloride (V; 0.01 mol) with Fe(II) Oxalate in DMF at 155-60° for 1 hr

Run	Molar ratio Halide:Fe(II)	Reaction Atmosphere	% yield of products	
			Ph ₃ CH	Ph ₃ C-OH
20 ^g	1:1	N ₂	14	79
21	1:0.5	N ₂	11	81
22	1:0.25	N ₂	7	86
23	1:1	O ₂	trace	93
24	1:1 (cyclohexene 0.10 mol was added)	N ₂	21	70

^g, Blank experiment of run 20 conducted in the absence of Fe(II) yielded triphenylcarbinol in 96% yield and no other product was detected.

The reactions of Co(II) with benzyl chloride (I), 4-nitrobenzyl bromide (II) or 9-bromofluorene (III) in DMF at 155-60° were also examined in order to make a comparative study with the corresponding reactions of Fe(II). The results obtained in the reactions of Co(II) with the halides (I), (II) and (III) are summarized in Table IV.4. Although each of the five benzylic halides (I)-(V), were recovered unchanged quantitatively from their respective DMF solutions kept under stirring for 1 hr

Table IV.4. Reaction of Benzylic Halides I, II and III

(Ar-CH-X; 0.01 mol) with Co(II) chloride (0.01 mol)
 in DMF at 155-60° under N₂ Atmosphere for 1 hr.
 (I = benzylchloride; II = 4-nitrobenzyl bromide;
 III = 9-bromofluorene).

Run	Halide	% yield of products				
		Ar-CH ₂ ↓	(Ar-CH) ₂ ↓	Ar-CHOH ↓	ArC=O ↓	Ar-CHNMe ₂ ↓
25 ^h	I	-	5	8	trace	6
26	II	trace	6	4	5	71
27 ⁱ	III	2	15	23	14	38

h, Starting halide remaining unreacted was 47% .

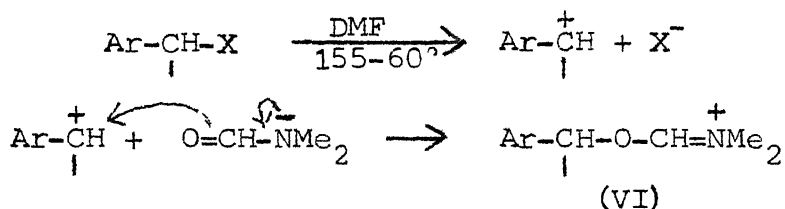
i, In the reaction with 9-bromofluorene, traces of bifluorenylidene (Ar-C=C-Ar) were also detected among the products.
 ↓ ↓

at room temperature, it is obvious from the data listed in Tables IV.1, IV.2, IV.3 and IV.4 that the solvent DMF reacts with these halides substantially at the reflux temperature giving benzylic alcohols (sometimes accompanied by the corresponding carbonyl compounds) and benzylic dimethylamines. The course of these reactions is significantly influenced by the addition of Fe(II) oxalate or Co(II) chloride.

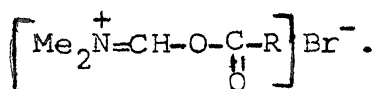
For the reactions occurring in the absence of Fe(II) and Co(II), it is conceivable that DMF acts as an ambident nucleophile. Substitution by the attack through oxygen atom of the DMF molecule would transform the benzylic halide (Ar-CH-X) into the intermediate species (VI) which is capable of yielding

The lower yields of the carbonyl compounds compared to those of the corresponding alcohols in the reactions of the halides (I), (II), (III), and (IV) in the absence of metal ions reflect a slower rate of consumption of the intermediate (VI) through the strained four-membered transition state. Substantially higher yields of oxygen-containing products in the blank experiments with secondary halides (III) and (IV) compared to that with the primary halide (I) under similar conditions suggests that the formation of the intermediate (VI) itself occurs by a S_N1 type process rather than a S_N2 type process (see Scheme IV.9):

SCHEME IV.9

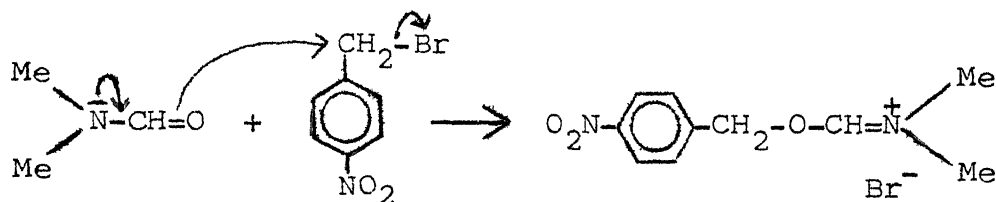


DMF is indeed, capable of bringing about ionization of certain alkyl⁵³ and acyl halides. Also, dipolar aprotic solvents are known to solvate cations strongly,⁵⁵⁻⁵⁹ hence leaving the counter anion free to act as nucleophile and lessening the influence of ion-pair formation. Acyl bromides are also strongly dissociated in DMF and form salts⁵⁴ formulated as

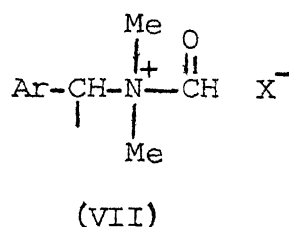


In the case of 4-nitrobenzyl bromide (II) where S_N1 type of ionization is rendered difficult by the presence of the nitro group in 4-position; nucleophilic attack by the oxygen atom of

DMF via a S_N2 type pathway would result in the formation of the intermediate corresponding to (VI):



Nucleophilic attack through the nitrogen atom of DMF leading to the intermediate species (VII) would be disfavoured due to



not only the attendant steric factors but also the requirement of placing a positive charge at the nitrogen atom adjacent to the positively charged carbon of the carbonyl group in (VII), particularly when a facile nucleophilic displacement path involving the oxygen atom of DMF leading to intermediate (VI) is available. Formation of the intermediate species (VII) which is inescapable for the production of benzylic dimethylamines in our blank reactions with the halides (I), (II), (III) and (IV) should, therefore, be taking place by a non-nucleophilic pathway. In this connection, a comparison of the results of the blank experiment involving benzyl chloride (I) with those involving 4-nitrobenzyl bromide (II) reveals the same kind of dramatic effect of the nitro group towards enhancing the yield of the benzylic dimethylamine as found by Kornblum and

coworkers⁶⁰ towards enhancing the yield of the C-alkylation product in the reaction of 4-nitrobenzyl bromide with the 2-nitropropanate anion. It is also known⁵¹ that the presence of electron withdrawing substituents at 4-position in 4-substituted-2-nitrohalobenzenes enhances the yield of 4-substituted-2-nitrodimethyl anilines in the reaction of the former with DMF (in the presence of CsF catalyst!). While the ability of 4-nitrobenzyl bromide to act as one electron oxidant is well established,⁶⁰ one electron oxidation of DMF giving radical-cation of DMF in an oxidising environment is also precedented.⁵¹

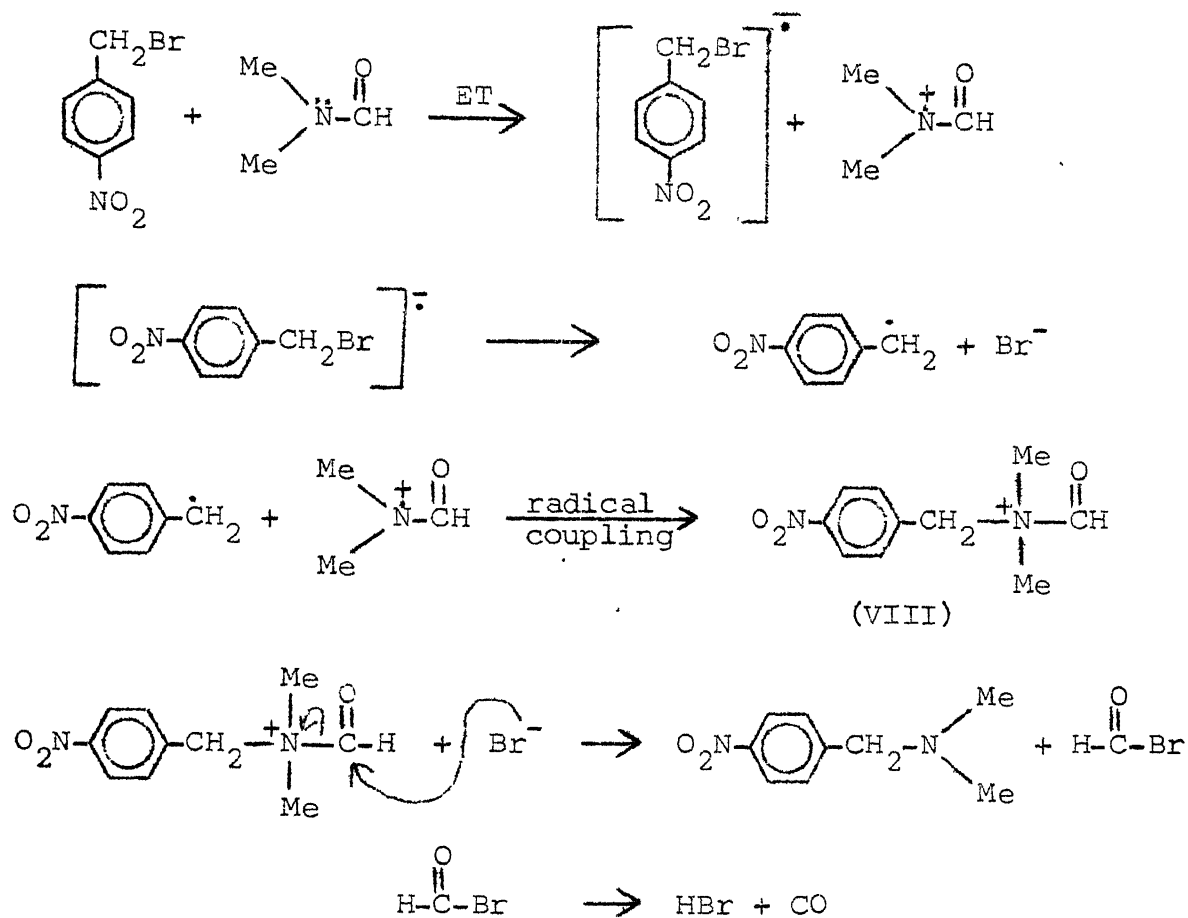
In view of the foregoing arguments, we suggest that in our blank reaction with 4-nitrobenzyl bromide (run 5; Table IV.1), the intermediate (VIII) corresponding to species (VII) is formed by an electron transfer process and 4-nitrobenzyl dimethylamine is produced from this intermediate subsequently (see Scheme IV.10).

The carbocations formed in the reactions of the halides (I), (III), and (IV) may, like 4-nitrobenzyl bromide oxidize DMF (in one of the available reaction pathways) ultimately giving benzylic dimethylamines as shown in Scheme IV.11.

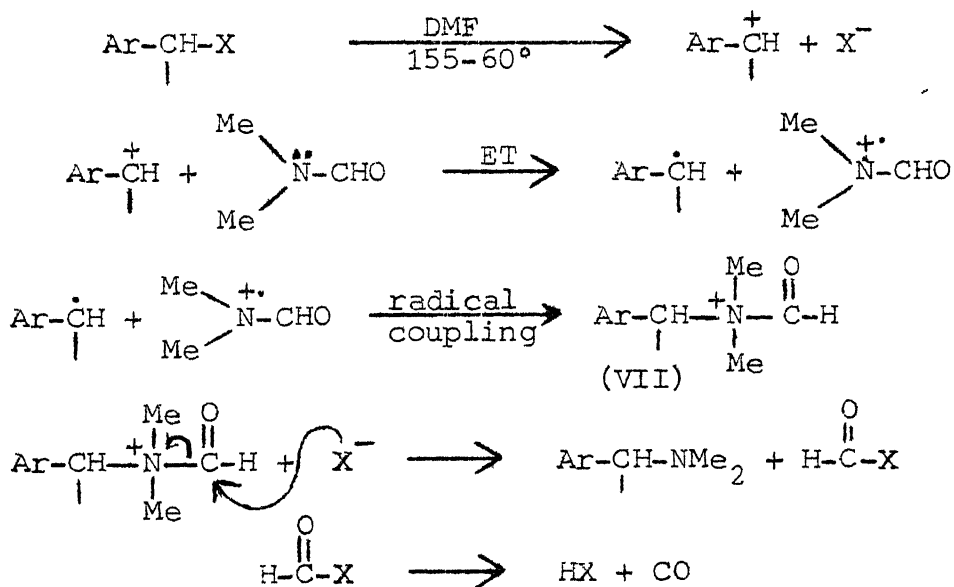
It is, however, evident from the data on the blank reaction with trityl chloride (V) that the stable triphenylmethyl carbocations are not reduced to radicals by DMF.

A close look at the experimental data on the reactions of the halides (I), (II), (III), (IV) and (V) shows that the course

SCHEME IV.10

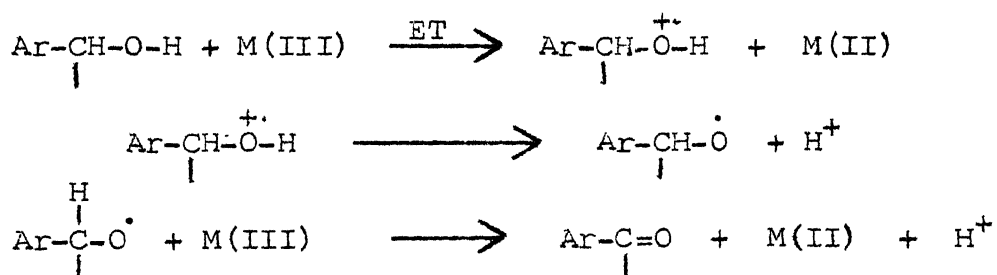


SCHEME IV.11



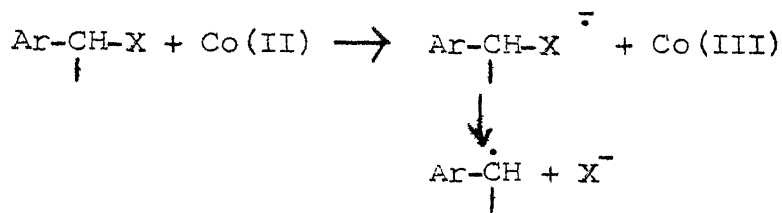
The effect of the highly oxidizing environment as provided by the oxygen atmosphere of run 4 (Table IV.1), is to increase the concentration of M(III) species via the oxidation of M(II). While increased concentration of M(III) species may tend to enhance the yield of benzylic dimethylamine by producing higher concentration of DMF radical-cations, it also oxidizes the benzylic radicals to carbocations (a process that tends to decrease the yield of the tertiary amine). Consequently, the additional quantity of carbocations help in producing more alcohol (than under N₂ atmosphere). An additional amount of alcohol would be produced via the trapping of benzylic radicals with molecular oxygen. Some of the alcohol is oxidized to the corresponding carbonyl compound when sufficient M(III) ions are present (see Scheme IV.13):

SCHEME IV.13



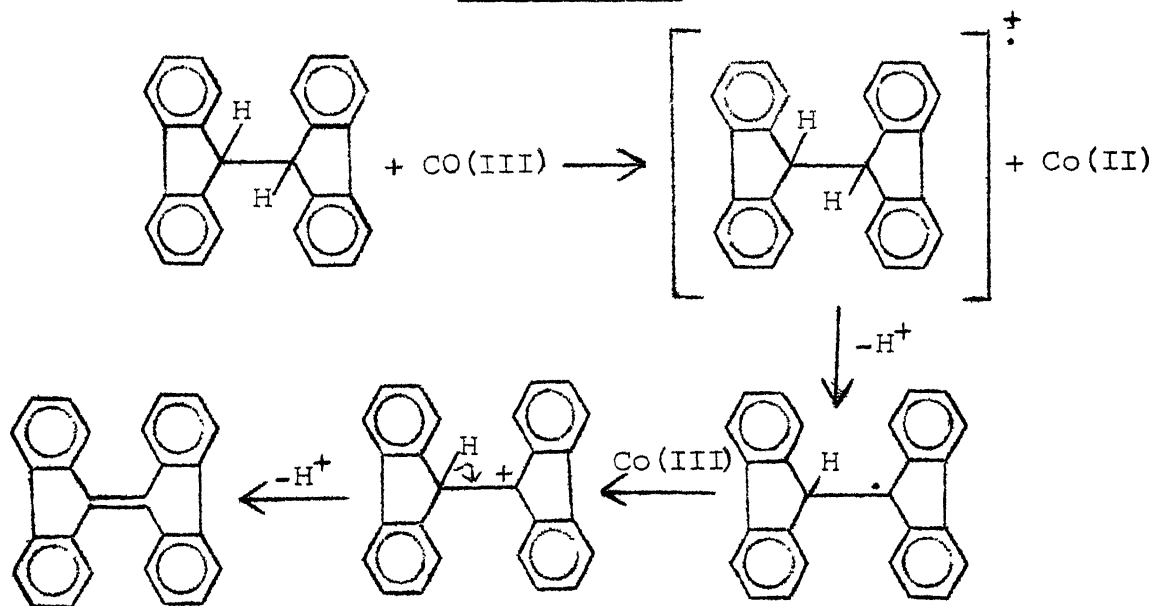
Indeed, a control experiment with 9-fluorenol and Co(III) under similar reaction conditions showed significant oxidation of 9-fluorenol to 9-fluorenone. At the same time, no noticeable reduction of 9-fluorenone with Co(II) to 9-fluorenol, was observed when a control experiment was carried out.

It appears that the Co(II) species is able to transfer one electron to the LUMO's of benzylic halides (I) and (III) also (see Table IV.4), resulting in the formation of benzylic radicals:



Cobalt(III) species so produced, oxidize DMF to give DMF radical-cations and also a part of the radicals to carbocations. Partial oxidation of the initially formed 9,9'-bifluorenyl to 9,9'-bifluorenylidene as seen in run 27 of Table IV.4 may also be rationalized by the use of Co(III) as outlined in Scheme IV.14.

SCHEME IV.14

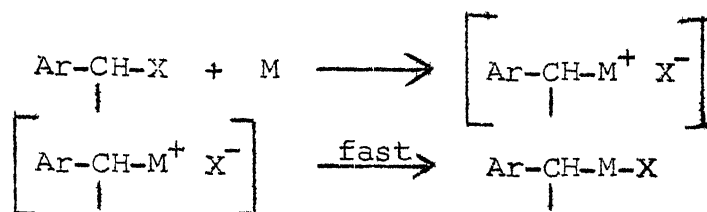


Electron transfer oxidations of hydrocarbons by Co(III) are known.⁶¹

An outer sphere electron transfer mechanism in the reduction of benzylic halides with Co(II) is also supported by the Hammett correlation of rate constants.⁶²

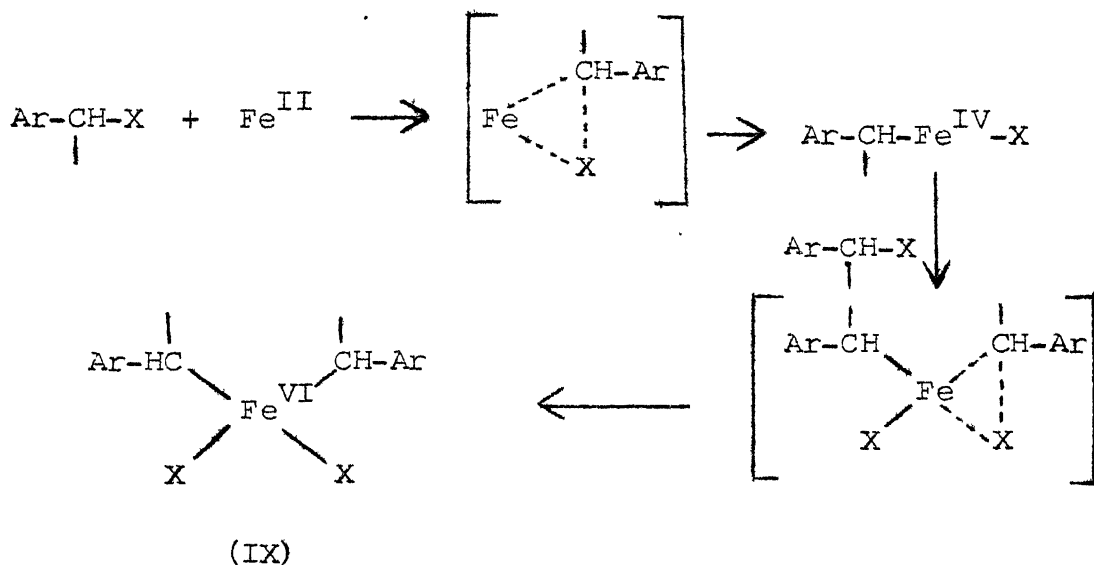
About the reduction of the halides (I), (III) and (IV) with Fe(II) species, no major mechanistic conclusions can be derived from the available data. However, the information listed in Table IV.2 appears to indicate that free radicals are not involved here. (For instance, compare last two pairs of the reactions with rest of the pairs.) The fact that the benzylic halides are consumed faster than the dimers are produced is indicative of the formation of an organoiron complex intermediate. The reduction of significantly more halide than expected on the basis of 1:1 stoichiometry of the halide to Fe(II) suggests that the organoiron complex intermediate is associated with more than one halide molecule for each Fe(II) species. The information given in the footnotes of the Table IV.2 also indicates that the organoiron complex intermediate is formed faster than the DMF assisted ionization of the organic halide takes place, Fe(II) thus suppresses the formation of products derived through carbocations in the blank experiments.

In view of the foregoing arguments it is likely that the suggested organoiron compound could arise by a non-radical oxidative addition mechanism. A conceivable S_N2 type, 2-centre concerted nucleophilic displacement mechanism of oxidative addition outlined below,



is not applicable in the present cases as the same would have been more facile with the primary halide (run 1, Table IV.1) than with the secondary halides examined in Table IV.2. It is, therefore, proposed that the oxidative addition in the present cases takes place by a 3-centre, concerted, frontside nucleophilic displacement mechanisms (Scheme IV.15):

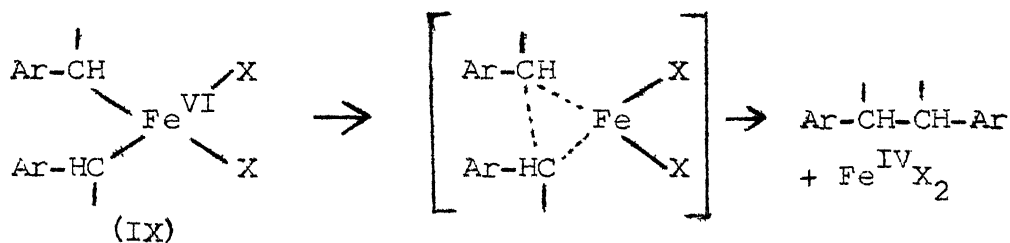
SCHEME IV.15



It is noteworthy in this connection that in a recent study on the reductive coupling of benzyl chloride in presence of $\text{Fe}_3(\text{CO})_{12}$ in benzene a broad NMR signal at δ 1.22 ppm assignable to the methylene group of unstable system PhCH_2Fe has been recorded.⁴⁴

The dimeric products of the type listed in Table IV.2 could arise from the organoiron compound (IX) by a homolytic process in the solvent cage; but a cage reaction if occurring at the temperature of our reactions (i.e. 155-60°C) would have allowed a part of the radicals to diffuse out of the cage giving some other radical-derived product(s).

In our opinion, a homolytic process leading to products via radical intermediates is not occurring; but a facile, concerted orbital symmetry allowed process results in the reductive coupling as is known for two alkyl ligands attached to a single metal center.³⁴ By implication, compound (IV) should have a tetrahedral structure.



Iron species in higher oxidation states could be converted into species in lower oxidation states by various permissible redox reactions including the electron donation from DMF. Formation of traces of bifuorenylidene in all the experiments of 9-bromofluorene(III) listed in Table IV.2 can be rationalized by the same set of steps as outlined in Scheme IV.14 with the only difference that Fe in a higher oxidation state, for example, Fe(III) is the oxidizing agent in place of Co(III). In a control experiment with Fe(III), 9,9'-bifuorenyl was actually found to give bifuorenylidene.

The reaction of trityl chloride in presence of Fe(II) may form the dimeric compound - hexaphenylethane by the same mechanism; but homolytic decomposition of the dimeric product expected to take place under the conditions employed by us results in the formation of triphenylmethyl radicals which are mainly oxidized to carbocations by the metal ions in higher oxidation states. Thus, triphenyl carbinol is formed by a nucleophilic attack route in major yield (Table IV.3). A small fraction of triphenylmethyl radicals which survive oxidation, abstract hydrogen atom from DMF giving triphenylmethane. In oxygen atmosphere, radicals are trapped by oxygen again forming triphenylcarbinol.

It should be noted, however, that a more rigorous delineation of mechanisms involving Co(II) and Fe(II) is not possible with the data at hand and the suggestions made here should be treated as tentative.

IV.4 Experimental

All the melting points were recorded using MEL-TEMP melting point apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer model-580 spectrophotometer. The products were identified by comparison of their IR spectra with those of the authentic samples, by TLC, melting points and mixed melting points. Literature melting points are cited from "Handbook of Chemistry and Physics," 50th edition, R.C. Weast (Ed.)

published by the Chemical Rubber Company, Cleaveland, Ohio, unless otherwise specified. Silica-gel (ase-India) was used for TLC analyses.

Starting Materials

Iron(II) oxalate (Veb Laborchemie Apolda, Germany) and cobalt(II) chloride (BDH) were used. Silica-gel (Acme's) of 100-200 Mesh size was used for column chromatography. Benzyl chloride (E. Merck) was used after distillation. 4-Nitrobenzyl bromide,⁶³ 9-bromofluorene,⁶⁴ benzhydryl chloride⁶⁵ and trityl chloride⁶⁶ were prepared by known methods. Fluorenone (Schuchard München, Germany) was used and 9-fluorenol was prepared as reported in literature.⁶⁷ Dimethylformamide (SDS) was used in all the reactions after drying as described below:

Preparation of Deaerated, dry N,N-Dimethylformamide

Dimethylformamide was kept over calcium chloride for twenty four hours after which it was decanted into a one-litre round bottomed flask. It was distilled at atmospheric pressure and the fraction distilling over a temperature range of 152-154°C was collected. DMF was deaerated by passing pure and dry nitrogen continuously for half an hour into the solvent contained in a one litre RB flask mounted over a magnetic stirring base.

Reaction of Benzyl Chloride with Fe(II); Molar ratio-1:1

In a 3-necked RB flask mounted over a magnetic stirring base, fitted with a condenser and a mercury trap were placed

benzyl chloride (1.26 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml). The flask was flushed with pure nitrogen for 10 min. after which the contents of the flask were heated in an oil-bath at 155-160°C for a period of one hour. The oil-bath was removed after this duration and the flask cooled to room temperature. The reaction mixture was worked up after adding to acidified water. The products were extracted with ether, the ethereal extract washed with an excess of water and dried over MgSO_4 (anhyd.). GLC analysis of the mixture of products using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of benzaldehyde in trace amount, benzyl chloride (0.872 g, ~69%), benzyl alcohol (0.075 g, ~7%) and bibenzyl (0.091 g, ~10%). The above reaction was repeated and the reaction mixture subjected to GLC analysis without work-up. In this way, formation of benzyl dimethylamine (0.027 g, ~2% - by calibration method) was also noticed.

Reaction of Benzyl Chloride with DMF

The above reaction was repeated using benzyl chloride (1.265 g, 0.01 mol) and 50 ml of dry DMF in the absence of iron salt under otherwise identical conditions. After cooling the reaction mixture to room temperature, it was subjected to GLC analyses using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Formation of benzyl alcohol (0.086 g, ~8%) and trace amounts of benzaldehyde and benzyl dimethylamine was thus indicated. No bibenzyl was indicated among the products.

Reaction of 4-Nitrobenzyl bromide with Fe(II); Molar ratio - 1:1

In a 3-necked round bottomed flask mounted over a magnetic stirring base and fitted with a condenser, a mercury trap and a gas passing adaptor, were placed 4-nitrobenzyl bromide (2.16 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml). The contents of the flask were flushed with dry nitrogen for ten minutes, and then heated over a temperature range of 155-160°C in an oil-bath. The heating was continued for 1 hr. after which the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction mixture was worked up after adding to acidified water. The products were extracted with solvent ether. The aqueous solution was made alkaline by adding aqueous sodium hydroxide when iron hydroxide separated as a precipitate. The precipitate was filtered off and washed with solvent ether 2-3 times. The aqueous filtrate was again extracted with solvent ether and the combined ethereal extracts washed with an excess of water and dried over anhydrous MgSO_4 . The product mixture was subjected to GLC analysis using 10% SE-30 on Crom-P (85-100 M) column of 2 m length which indicated the presence of 4-nitrotoluene (0.137 g, ~10%), 4-nitrobenzaldehyde (0.060 g, ~4%), 4-nitrobenzylalcohol (0.046 g, ~3%) and 4-nitrobenzyl dimethylamine (1.116 g, ~62%) by calibration method. The ether extract was then concentrated and charged on a silica-gel column. Elution of the column with benzene gave 4,4'-dinitrobibenzyl (0.215 g, ~16%) which was identified by a comparison of its IR spectrum

with that of an authentic sample, melting point and mixed melting point technique.

Reaction of 4-Nitrobenzyl bromide with Fe(II); Molar ratio - 1:0.5

The above reaction was repeated using 4-nitrobenzyl bromide (2.16 g, 0.01 mol), iron(II) oxalate (0.90 g, 0.005 mol) and 50 ml of dry DMF under otherwise similar conditions. The distribution of products in the reaction mixture was found to be 4-nitrotoluene (0.0685 g, ~5%), 4-nitrobenzaldehyde (0.09 g, ~6%), 4-nitrobenzylalcohol (0.183 g, ~12%), 4-nitrobenzyl-dimethylamine (0.864 g, ~48%) and 4,4'-dinitrobibenzyl (0.095 g, ~7%) using the method described in the previous experiment.

Reaction of 4-Nitrobenzyl bromide with Fe(II); Molar ratio - 1:1
(under O₂ atmosphere)

In a 100 ml 3-necked RB flask, 4-nitrobenzyl bromide (2.16 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml) were taken. The flask was fitted with a condenser, a mercury trap and a gas passing adaptor. The gas inlet was connected to an oxygen gas cylinder and the slow bubbling of the gas was started. The flask was then heated in an oil-bath over a temperature range of 155-160°C for 1 hr. After this period the oil-bath was removed and the flask cooled to room temperature. The reaction mixture was worked up in the manner as described in reaction (2) above, and the product distribution by the method detailed in the same reaction was found to be

4-nitrobenzaldehyde (0.347 g, \sim 23%), 4-nitrobenzylalcohol (0.092 g, \sim 6%) and 4-nitrobenzyltrimethylamine (1.098 g, \sim 61%).

Reaction of 4-Nitrobenzyl bromide with DMF

4-Nitrobenzyl bromide (2.16 g, 0.01 mol) and 50 ml of dry DMF were taken in a three-necked RB flask (in the absence of the metal salt). The contents of the flask were flushed with dry N_2 for 10 min. and then heated in an oil-bath over a temperature range of 155-160°C for 1 hr. After cooling to room temperature, the reaction mixture was subjected to GLC analysis as such. The GLC analyses using 10% SE-30 on Crom-F (85-100 M) column of 2 m length indicated the presence of 4-nitrobenzaldehyde (0.060 g, \sim 4%), 4-nitrobenzylalcohol (0.122 g, \sim 8%) 4-nitrobenzyltrimethylamine (0.414 g, \sim 23%) and unreacted 4-nitrobenzyl bromide (1.23 g, \sim 57%) in the mixture of products.

Reaction of 9-Bromofluorene with Fe(II); Molar ratio - 1:2

In a 100 ml 3-necked RB flask, mounted over a magnetic stirring base, were placed 9-bromofluorene (2.45 g, 0.01 mol) iron(II) oxalate (3.60 g, 0.02 mol) and dry DMF (50 ml). The flask was fitted with a gas inlet tube, a condenser and a mercury trap. The flask was flushed with dry N_2 for 10 min. and then heated in an oil-bath over a temperature range of 155-160°C for a period of 1 hr. After this period, the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction mixture was worked up by adding to acidified water when a fluffy solid precipitated. The solid

was filtered at pump and dried. The yield of the crude solid was 1.56 g (~95%). A part of the solid was recrystallized from alcohol and identified as 9,9'-bifluorenyl (m.p. 248°, lit. m.p. 247°C). The structure was confirmed by comparison of its IR spectrum with that of an authentic sample and mixed melting point technique. Thin layer chromatography of the mother liquor showed traces of bifluorenylidene and 9-fluoreno1. In a repeat experiment carried out to determine the formation of fluorene, the product mixture was charged on a silica-gel column. Elution of the column using petroleum ether (b.p. 60-80°) did not yield any fluorene.

Reaction of 9-Bromofluorene with Fe(II); Molar ratio - 1:1

The above reaction was repeated using 9-bromofluorene (2.45 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol), and dry DMF (50 ml) under otherwise similar conditions. Product distribution was determined to be 9,9'-bifluorenyl (1.56 g,

95%) and trace amounts of 9-fluoreno1 and bifluorenylidene by the method detailed above.

The above reaction was repeated in order to have a qualitative idea about the rate of formation of the dimer. The aliquots were removed at intervals of 15 min. and added to acidified water. A qualitative study of the products on tlc indicated that though more of the halide had disappeared, comparatively less of the dimer formation took place.

Reaction of 9-Bromofluorene with DMF

9-Bromofluorene (2.45 g, 0.01 mol) and dry DMF (50 ml) were kept in a 100 ml 3-necked flask and heated in an oil-bath over a temperature range of 155-160° under an atmosphere of N₂ for one hour. The reaction mixture was worked up by adding to water. The products were extracted with ether, the extract washed with water, dried over MgSO₄ (anhyd.) and concentrated to give a mixture which was analysed by chromatography using a silica-gel column and petroleum ether (b.p. 60-80°) eluant. The products obtained were fluorenyldimethylamine (0.29 g, ~14%), fluorenone (0.185 g, ~11%) and 9-fluorenol (0.30 g, ~17%), besides unreacted 9-bromofluorene.

Reaction of 9-Bromofluorene with Fe(II); Molar ratio 1:0.5

This reaction with new molar ratio of the reactants using 9-bromofluorene (2.45 g, 0.01 mol) and iron(II) oxalate (0.90 g, 0.005 mol) in DMF (50 ml) was conducted along the same lines as described for the reactants in equimolar ratio. The product distribution determined in the same way was found to be 9,9'-bifluorenyl (1.40 g, ~85%) and traces of 9-fluorenol and bifluorenylidene.

Reaction of 9-Bromofluorene with Fe(II); Molar ratio - 1:0.25

The reaction of 9-bromofluorene (2.45 g, 0.01 mol) and iron(II) oxalate (0.45 g, 0.0025 mol) in 50 ml of dry DMF was conducted in the manner described in the previous experiment. On work-up and analysis in the usual manner, 9,9'-bifluorenyl

was found to be 0.726 g (44%). Thin layer chromatography also indicated the presence of trace amounts of 9-fluorenol and bifluorenylidene.

Reaction of 9-Bromofluorene with Fe(II); Molar ratio - 1:1 —
Reaction time 12 hr

The reaction of 9-bromofluorene (2.45 g, 0.01 mol) with iron(II) oxalate (1.80 g, 0.01 mol) in 50 ml of dry DMF was carried out for a period of 12 hr over a temperature range of 155-160°C. After this period, the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction mixture was worked up by adding to acidified water. 9,9'-Bifluorenyl (1.49 g, ~ 90%) , 9-fluorenol and bifluorenylidene both in traces were indicated as the products.

Reaction of 9-Bromofluorene with Fe(II), Molar ratio 1:1 (under
O₂ atmosphere)

In a 100 ml 3-necked flask were placed 9-bromofluorene (2.45 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml). The flask was flushed with oxygen gas for 10 min. The contents of the flask were then heated on an oil-bath over a temperature range of 155-160° for a period of 1 hr. The reaction mixture was worked up in the usual manner when the products were found to be 9,9'-bifluorenyl (1.51 g, ~ 92%) and 9-fluorenol and bifluorenylidene both in traces.

Reaction of 9-Bromofluorene with Fe(II); Molar ratio - 1:1
(in presence of cyclohexene)

In a 100 ml 3-necked RB flask mounted over a magnetic stirring base and fitted with a condenser, a mercury trap and a gas passing adaptor, were placed 9-bromofluorene (2.45 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol), cyclohexene (1.23 g, 0.015 mol) and dry DMF (50 ml). The reaction was carried out for 1 hr under nitrogen atmosphere over a temperature range of 155-160°. After work-up, presence of 9,9'-bifluorenyl (1.55 g, ~94%) and 9-fluorenol and bifluorenylidene (both in trace amounts) was indicated.

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:2

In a 100 ml 3-necked RB flask, mounted over a magnetic stirring base and fitted with a mercury trap, a condenser and a gas passing adaptor, were placed benzhydryl chloride (2.02 g, 0.01 mol), iron(II) oxalate (3.60 g, 0.02 mol) and dry DMF (50 ml). The flask was flushed with dry N₂ for 10 min. and then heated in an oil-bath over a temperature range of 155-160° for a period of 1 hr. The oil-bath was then removed and the flask cooled to room temperature. The reaction mixture was worked up by adding to acidified water when a white solid precipitated. The solid was filtered at the pump, washed with a little ether and dried. The solid was identified as 1,1,2,2-tetraphenylethane m.p. 212°C, Lit. m.p. 212.5°C (1.42 g, ~85%) by the mixed m.p. technique and comparison of its IR spectrum with that of an authentic sample. The mother liquor was extracted with ether.

After concentration of the ether extract, tlc showed the presence of a trace amount of benzhydrol.

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:1

The above reaction was repeated using benzhydryl chloride (2.02 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml) under otherwise the same conditions as described for above experiments. 1,1,2,2-Tetraphenylethane (1.435 g, ~86%) and traces of benzhydrol were indicated among the products.

The above reaction was repeated and aliquots removed at intervals of 15 min. and added to acidified water. The products were extracted with ether and dried (MgSO_4). Concentration of the ethereal extract followed by tlc analysis of the mixture indicated qualitatively the slower rate of formation of the dimer compared to the disappearance of the halide.

Reaction of Benzhydryl chloride with DMF

The above reaction was repeated with benzhydryl chloride (2.02 g, 0.01 mol) and dry DMF (50 ml) in the absence of metal salt under otherwise identical conditions. GLC analysis of the cooled reaction mixture using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of benzophenone (0.125 g, ~7%), benzhydrol (0.295 g, ~16%) and benzhydryldimethylamine (0.126 g, ~6%) among the products (calibration method), besides unreacted starting halide.

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:0.5

This reaction with new molar ratio of reactants using benzhydryl chloride (2.02 g, 0.01 mol), iron(II) oxalate (0.90 g, 0.005 mol) and dry DMF (50 ml) was conducted in the usual manner. The product analysis by the method as described above indicated the formation of 1,1,2,2-tetraphenylethane (1.38 g, ~83%) and a trace amount of benzhydrol.

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:0.25

The reaction of benzhydryl chloride (2.02 g, 0.01 mol) with iron(II) oxalate (0.45 g, 0.0025 mol) in dry DMF (50 ml) was conducted in the same way as described for the above experiments. Work-up of the reaction mixture and product analysis in the manner described previously indicated the formation of 1,1,2,2-tetraphenylethane (0.68 g, ~40%) and benzhydrol (trace amount).

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:1 —
Reaction time 12 hr.

The reaction of benzhydryl chloride (2.02 g, 0.01 mol) and iron(II) oxalate (1.80 g, 0.01 mol) in 50 ml of dry DMF was carried out in the manner described above for a period of 12 hr. After cooling the reaction mixture to room temperature, it was worked up in the usual manner. The product analysis indicated the formation of 1,1,2,2-tetraphenylethane (1.43 g, ~86%) and benzhydrol (trace amount).

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:1
(under O₂ atmosphere)

In a 100 ml 3-necked RB flask were placed benzhydryl chloride (2.02 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml). The flask was flushed with oxygen gas for 10 min. and then heated in an oil-bath over a temperature range of 155-160° for a period of 1 hr. After this period, the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction mixture was worked up in the usual manner and the products formed were 1,1,2,2-tetraphenylethane (1.40 g, ~84%) and benzhydrol (trace amount).

Reaction of Benzhydryl chloride with Fe(II); Molar ratio - 1:1
(in presence of cyclohexene)

In a 100 ml 3-necked flask, mounted over a magnetic stirring base and fitted with a mercury trap, a condenser and gas passing adaptor, were placed benzhydryl chloride (2.02 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol), cyclohexene (1.23 g, 0.015 mol) and dry DMF (50 ml). The flask was flushed with dry nitrogen and the contents of the flask heated in an oil-bath over a temperature range of 155-160°C for 1 hr. After this period, the oil-bath was removed and the contents of this flask cooled to room temperature. After working up the reaction mixture in the usual manner, formation of 1,1,2,2-tetraphenylethane (1.38 g, ~83%) and benzhydrol (trace amount) was indicated.

Reaction of Trityl chloride with Fe(II); Molar ratio - 1:1

In a 100 ml 3-necked RB flask, mounted over a magnetic stirring base and fitted with a mercury trap, a condenser and a gas passing adaptor, were placed trityl chloride (2.785 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml). The flask was flushed with dry nitrogen for 10 min. and then heated in an oil-bath over a temperature range of 155-160°C for 1 hr. After this period, the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction was worked up by adding to acidified water. The products were extracted thrice with solvent ether. The combined ethereal extracts after washing with water and drying over MgSO_4 (anhyd.) was concentrated to give a product mixture that showed two spots on tlc. The mixture was charged on a silica-gel column. Elution of the column with petroleum ether (b.p. 60-80°) and petroleum ether (b.p. 60-80°): benzene mixture 50:50 (v/v) gave triphenylmethane (0.340 g, ~14%, m.p. 94°, lit. m.p. 94°C) and triphenylcarbinol (2.05 g, ~79%, m.p. 164°, lit. m.p. 164.2°C). These compounds were identified by comparison of their IR spectra with those of the authentic samples, by mixed melting point technique, TLC and C, H analyses.

Reaction of Trityl chloride with DMF

In a 100 ml 3-necked flask were placed trityl chloride (2.785 g, 0.01 mol) and dry DMF (50 ml). The flask was flushed with dry N_2 for 10 min. and the reaction conducted in the usual

manner for a period of one hour. On work-up in the usual manner, triphenylcarbinol (2.49 g, 96%) was obtained. No other product was detected.

Reaction of Trityl chloride with Fe(II); Molar ratio - 1:0.5

The reaction with new molar ratio was repeated using trityl chloride (2.785 g, 0.01 mol), iron(II) oxalate (0.90 g, 0.005 mol) and dry DMF (50 ml) under otherwise identical conditions. The reaction was worked up as described above. Separation of products on a silica-gel column using petroleum ether (b.p. 60-80°) and petroleum ether (b.p. 60-80°):benzene mixture 50:50 (v/v) yielded triphenylmethane (0.26 g, ~11%) and triphenylcarbinol (2.10 g, ~81%).

Reaction of Trityl chloride with Fe(II); Molar ratio - 1:0.25

The above reaction was repeated using trityl chloride (2.785 g, 0.01 mol), iron(II) oxalate (0.45 g, 0.0025 mol) and dry DMF (50 ml) under otherwise similar conditions. Separation of products in the usual manner yielded triphenylmethane (0.170 g, ~7%) and triphenylcarbinol (2.24 g, ~86%).

Reaction of Trityl chloride with Fe(II); Molar ratio - 1:1 (under O₂ atmosphere)

In a 100 ml 3-necked flask were placed trityl chloride (2.785 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol) and dry DMF (50 ml). The flask was connected to an oxygen gas cylinder through a gas passing adaptor. Oxygen was bubbled

in the solution continuously. The contents of the flask were heated in an oil-bath over a temperature range of 155-160° for 1 hr. After this period, the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction was worked up in the usual manner. Separation of products on a silica-gel column using petroleum ether (b.p. 60-80°) and petroleum ether (b.p. 60-80°):benzene mixture 50:50 (v/v) as eluants yielded traces of triphenylmethane and (2.42 g, ~93%) of triphenylcarbinol.

Reaction of Trityl chloride with Fe(II); Molar ratio - 1:1 (in presence of cyclohexene)

In a 100 ml 3-necked flask were placed trityl chloride (2.785 g, 0.01 mol), iron(II) oxalate (1.80 g, 0.01 mol), cyclohexene (8.20 g, 0.1 mol) and dry DMF (50 ml). The flask was flushed with dry N₂ for 10 min. and the reaction conducted under otherwise identical conditions by heating for 1 hr. Separation of products in the usual manner gave triphenylmethane (0.500 g, ~21%) and triphenylcarbinol (1.82 g, ~70%).

Reaction of Benzyl chloride with Co(II); Molar ratio - 1:1

In a 100 ml 3 necked flask, mounted over a magnetic stirring base and fitted with a condenser, a mercury trap and a gas passing adaptor were placed benzyl chloride (1.265 g, 0.01 mol), Co(II)Cl₂ (1.30 g, 0.01 mol) and dry DMF (50 ml). The contents of the flask were flushed with dry N₂ for 10 min. and then heated in an oil-bath over a temperature range of 155-160°C for

a period of 1 hr. The oil-bath was then removed and the mixture in the flask cooled to room temperature. The reaction mixture was subjected to GLC as such. GLC analyses using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of benzaldehyde (trace amount), benzyl alcohol (0.086 g, ~8%), unreacted benzyl chloride (0.594 g, ~47%), benzyldimethylamine (0.081 g, ~6%) and bibenzyl (0.045 g, ~5%) by calibration method.

Reaction of 4-Nitrobenzyl bromide with Co(II); Molar ratio - 1:1

4-Nitrobenzyl bromide (2.16 g, 0.01 mol), Co(II)Cl_2 (1.30 g, 0.01 mol) and dry DMF (50 ml) were placed in a 100 ml 3-necked flask mounted over a magnetic stirring base and fitted with a mercury trap, a condenser and a gas passing adaptor. The flask was flushed with dry nitrogen and the contents of the flask heated in an oil-bath over a temperature range of 155-160° for 1 hr. After this period, the flask was cooled to room temperature and the mixture subjected to GLC analysis. The GLC analysis of the reaction mixture using 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of 4-nitrotoluene (trace amount), 4-nitrobenzaldehyde (0.076 g, ~5%), 4-nitrobenzylalcohol (0.061 g, ~4%) and 4-nitrobenzyldimethylamine (1.278 g, ~71%) by calibration method. The reaction mixture was then worked up by adding to acidified water. The products were extracted with solvent ether. The ethereal extract was washed with water and dried over MgSO_4 (anhyd.). After

concentration of the dried ethereal extract, the mixture was charged on a silica-gel column. Elution of the column with benzene gave 4,4'-dinitrobibenzyl (0.082 g, ~6%). This was confirmed by its m.p., mixed m.p. and comparison of IR spectrum with that of an authentic sample.

Reaction of 9-Bromofluorene with Co(II); Molar ratio - 1:1

9-Bromofluorene (2.45 g, 0.01 mol), Co(II)Cl_2 (1.30 g, 0.01 mol) and dry DMF (50 ml) were placed in a flask mounted over a magnetic stirring base under an atmosphere of nitrogen. The flask was heated in an oil-bath over a temperature range of 155-160°C for 1 hr. After this period, the oil-bath was removed and the contents of the flask cooled to room temperature. The reaction mixture was worked up after adding to acidified water. The products were extracted with solvent ether. The aqueous layer was made just alkaline and again extracted with ether. The combined ethereal extracts were washed with water and dried over MgSO_4 (anhyd.) and then concentrated to give a mixture which showed six spots on tlc. The mixture was charged on a silica-gel column. Elution of the column with petroleum ether (b.p. 60-80°), petroleum ether (b.p. 60-80°): benzene mixture 50:50 (v/v) and benzene gave fluorene (0.033 g, ~2%), 9,9'-bifluorenyl (0.247 g, ~15%), bifluorenylidene (trace amount), fluorenone (0.252 g, ~14%), 9-fluorenol (0.415 g, ~23%) and 9-fluorenyldimethylamine (0.79 g, ~38%).

Reaction of 9-Fluorenol with Co(III)

In a 100 ml 3-necked flask, mounted over a magnetic stirring base, were placed 9-fluorenol (1.82 g, 0.01 mol), $(\text{Co en}_2\text{Cl}_2)^+\text{Cl}^-$ (2.86 g, 0.01 mol; where en = ethylenediamine) and 50 ml of dry DMF. The flask was flushed with dry N_2 for 10 min. and heated in an oil-bath over a temperature range of 155-160°C for 1 hr. The oil-bath was removed after this period and the reaction mixture cooled to room temperature. The reaction was worked up after adding it to water. The products were extracted with solvent ether, the ethereal extract washed with water and dried over MgSO_4 (anhyd.). On concentration of the ethereal extract, a concentrate was obtained which on tlc showed two spots corresponding to fluorenone and 9-fluorenol. The mixture was charged on a silica-gel column. Elution of the column with petroleum ether (b.p. 60-80°) followed by benzene yielded fluorenone (0.230 g, ~13%) and unreacted 9-fluorenol (1.495 g, ~83%). The products were identified by m.p., mixed m.p. technique and comparison of their IR spectra with those of the authentic samples.

Reaction of Fluorenone with Co(II)

In a 3-necked flask, mounted over a magnetic stirring base were placed fluorenone (1.80 g, 0.01 mol), Co(II)Cl_2 (1.30 g, 0.01 mol) and dry DMF (50 ml). The reaction was conducted in the manner outlined above for 1 hr under N_2 atmosphere. The reaction mixture was worked up after adding to acidified

water and the products separated on a silica-gel column by elution with petroleum ether (b.p. 60-80°) and benzene. Unreacted fluorenone (1.725 g, ~96%) and 9-fluorenol (0.035 g, ~2%) were obtained in this manner.

Reaction of 9,9'-Bifluorenyl with Co(III)

9,9'-Bifluorenyl (1.65 g, 0.005 mol) ($\text{Co en}_2\text{Cl}_2$)⁺Cl⁻ (2.86 g, 0.01 mol; where en = ethylenediamine) and dry DMF (50 ml) were placed in a 100 ml 3-necked RB flask mounted over a magnetic stirring base. The flask was heated in a oil-bath over a temperature range of 155-160° for 1 hr under an atmosphere of nitrogen. After this period, the oil-bath was removed and the reaction mixture worked up after cooling and addition to acidified water. TLC of the crude mixture showed spots corresponding to 9,9'-bifluorenylidene and 9,9'-bifluorenyl.

Reaction of 9,9'-Bifluorenyl with Fe(III)

9,9'-Bifluorenyl (1.65 g, 0.005 mol) and iron(III) nitrate (3.50 g, 0.01 mol) in a total of 50 ml of dry DMF were taken in a flask and heated in an oil-bath over a temperature range of 155-160°C for a period of 1 hr under an atmosphere of nitrogen. After this period, the oil-bath was removed and the reaction mixture worked up after addition to acidified water. TLC of the crude product mixture indicated spots corresponding to 9,9'-bifluorenylidene and 9,9'-bifluorenyl.

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CHAPTER V

ROLE OF COBALT CATALYSTS IN THE REACTIONS OF GRIGNARD REAGENTS WITH ORGANIC HALIDES

V.1 Abstract

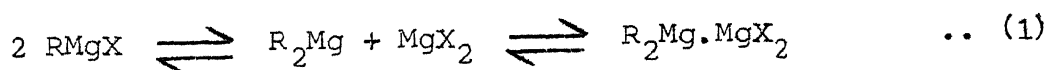
Reactions of benzyl magnesium chloride and phenyl magnesium bromide with several organic halides viz. benzyl chloride, benzhydryl chloride, trityl chloride, 9-bromofluorene and bromobenzene in presence of catalytic amounts of Co(II) or Co(III) compounds in THF under nitrogen atmosphere have been compared with the corresponding uncatalysed reactions. Cobalt catalysts have been found to enhance the yields of homo-coupling products derived from both components (i.e. Grignard reagent as well as organic halide) at the expense of the cross-coupling products. Based on the observations of a large number of reactions, a new chain mechanism involving Co^{I} species as the active catalyst in all the reactions (whether initial catalyst is Co^{II} or Co^{III}) has been suggested. The role of Co^{I} species as a supernucleophile has been highlighted. A clear distinction between Co^{I}

species suggested here and metallic cobalt (suggested in the literature earlier) with regard to the actual active catalyst in these reactions has not been possible. Free radicals have been proposed as immediate precursors of all dimeric products.

V.2 Introduction

The discovery of Grignard reagents, reported in 1900 by Victor Grignard¹ has been one of the major events in the history of chemistry. So great is the importance of Grignard reagents that the discoverer V. Grignard was awarded the Nobel prize in Chemistry in 1912 for the discovery and extensive work on this reagent.²⁻³ In spite of its tremendous synthetic importance, our understanding of the nature and structure of this reagent in solution and mechanisms of its reactions have progressed at a very slow rate. Though its structure is commonly written as RMgX, the reagent is actually much more complicated.⁴

Schlenk and Schlenk⁵ proposed that in solution, RMgX is in equilibrium with R_2Mg (Eq. 1):

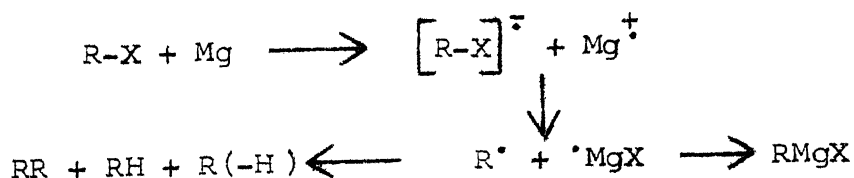


Rundle and coworkers⁶ demonstrated with the help of X-ray studies on solids crystallized from Grignard solutions that it has got a monomeric structure with each RMgX associated to two ether molecules. X-ray data after complete removal of ether showed⁷ the absence of any RMgX; but demonstrated the presence

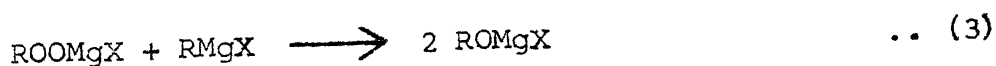
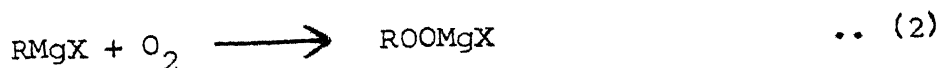
of a mixture of R_2Mg and MgX_2 . Measurements on the boiling point elevation and freezing point depression have shown⁸ that Grignard reagents prepared from alkyl bromides and iodides exist as monomeric species, in diethyl ether at lower concentrations ($\leq 0.1M$) and in THF at all concentrations. That the Schlenk equilibrium lies far to the left was shown by heat evolution study on mixing equimolar quantities of R_2Mg and MgX_2 .⁹

The formation of Grignard reagents itself from alkyl halides and magnesium metal has been recently reported to proceed by electron transfer from magnesium metal to alkyl halide¹⁰⁻¹³ (Scheme V.1):

SCHEME V.1



Grignard reagents undergo several types of reactions. Many of these reactions show characteristics of homolytic processes.^{3, 14-21} The reaction of Grignard reagents with oxygen has been known for a long time^{22, 23} (Eqs. 2 and 3):



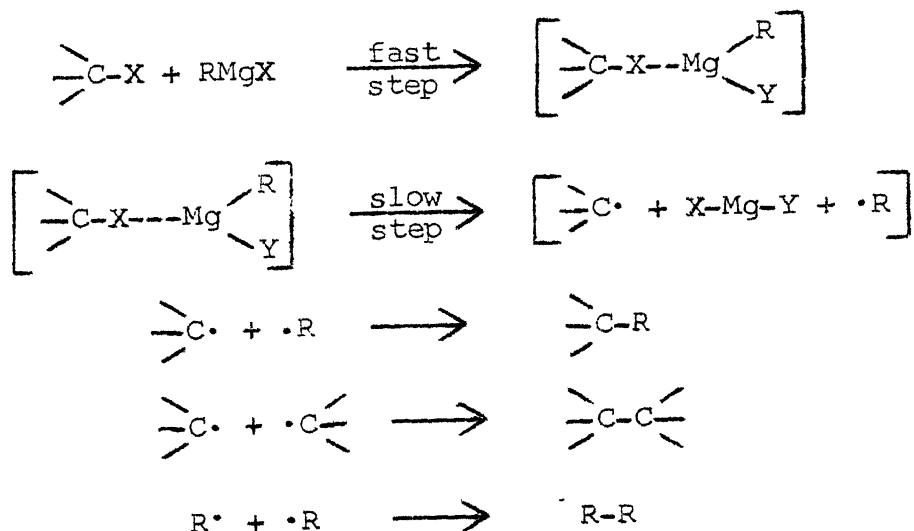
Recent studies have proved the involvement of free radicals^{14, 24} in these reactions which were previously believed to

be taking place through an ionic mechanism.²⁵ Free radical pathways have been indicated for both the steps²⁶⁻³¹ (Eqs. 2 and 3).

The mechanism of the reaction of Grignard reagents with ketones is not well understood. The exact nature of alkyl transfer from the Grignard reagent to the ketone, whether it proceeds by a polar or a single electron transfer has been a source of considerable speculation;³² but an electron transfer mechanism in the reactions of Grignard reagents with certain carbonyl compounds is now well recognized.

Singh and coworkers³³ have proposed electron transfer as the first step in the reaction of Grignard reagents with alkyl halides according to Scheme V.2:

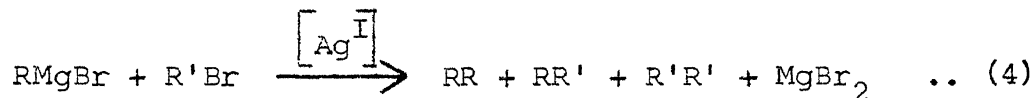
SCHEME V.2



Transition metal catalysts have been found to play significant roles in the formation of aromatic pinacols and

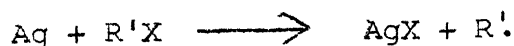
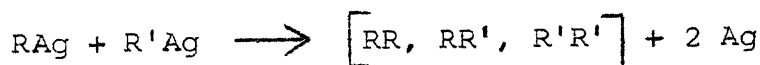
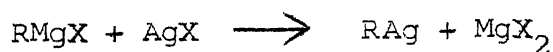
hydrols during Grignard reagent addition to ketones.³⁴ Transition metals have also been used in the cross coupling of Grignard reagents with organic halides.

The coupling of a Grignard reagent with an alkyl halide catalysed by silver affords a mixture of three alkyl dimers (Eq. 4) when dissimilar alkyl groups are employed.



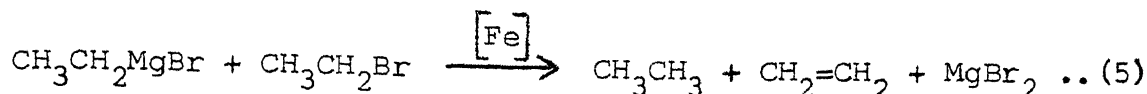
The scrambling of alkyl groups in the coupled products is not due to prior alkyl exchange between the Grignard reagent and the organic halide. Scheme V.3 summarizes the pathway proposed for the catalytic coupling reaction.³⁵

SCHEME V.3



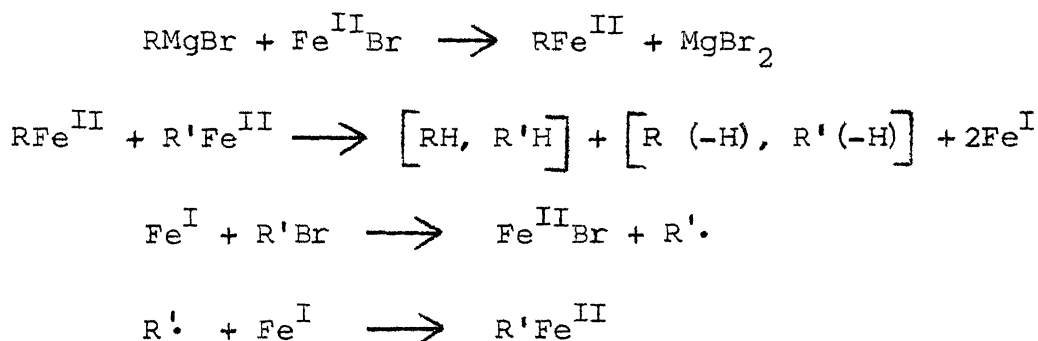
Grignard reagents, in the presence of iron species, behave quite differently from that observed with silver. Disproportionation, not coupling, of alkyl groups occurs as a result of iron-catalysed reaction of Grignard reagents with alkyl halides. Thus, a mixture of alkanes and alkenes, and

no significant amounts of alkyl dimers, are obtained³⁶ (Eq.5):



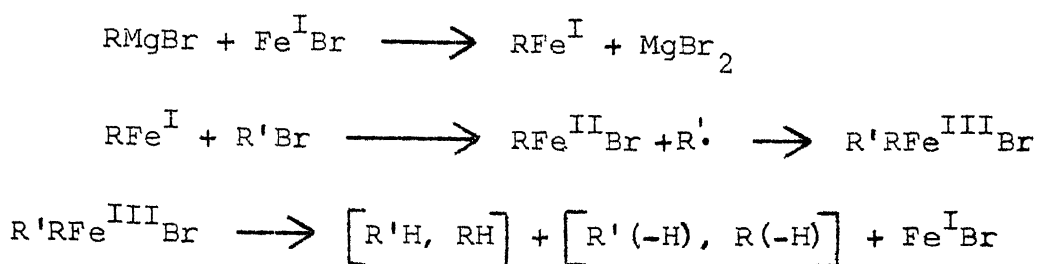
Stoichiometry studies³⁷ and ESR studies of the iron product³⁸ suggest that a paramagnetic iron(I) species is the active catalyst. The order of reactivities of alkyl bromides and the kinetics of disproportionation are the same as found in the silver catalysed coupling and therefore, suggest a similar mechanism³⁶ (Scheme V.4):

SCHEME V.4

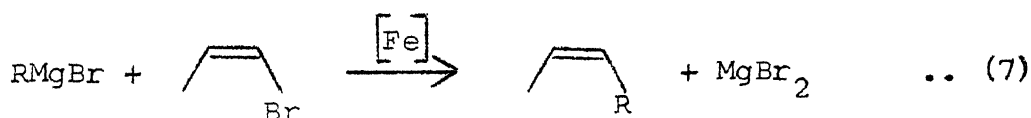
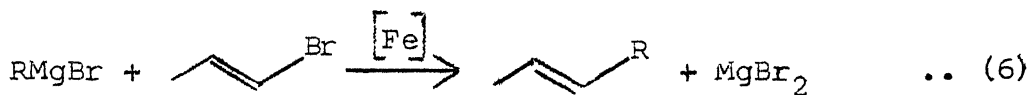


The mixtures of all four alkanes and alkenes derived from the reaction of Grignard reagents and organic halides utilizing different alkyl groups arise from the decomposition of organo-iron species in second step of Scheme V.4.

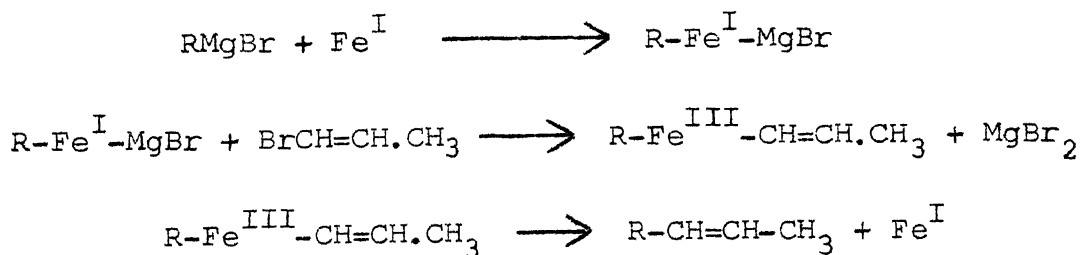
Disproportionation may also proceed from a dialkyl iron(II) species as in the third step of Scheme V.5. Such a disproportionation leads to an alternative mechanism for catalysis (Scheme V.5):

SCHEME V.5

Scheme V.5 is basically the same as Scheme V.4. The difference lies in the organoiron species which readily undergo disproportionation. However, under the same conditions, vinylic halides undergo cross coupling even with secondary and tertiary alkylmagnesium halides.³⁹ The cross-coupling proceeds with stereospecificity⁴⁰ (Eqs. 6 and 7):



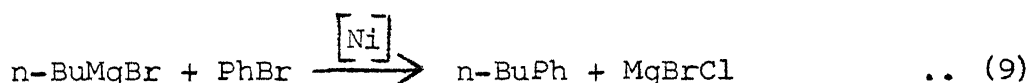
The mechanism proposed for these reactions is shown in Scheme V.6:

SCHEME V.6

This is a cyclic mechanism. In order to maintain stereospecificity, the oxidative addition of bromopropene in second

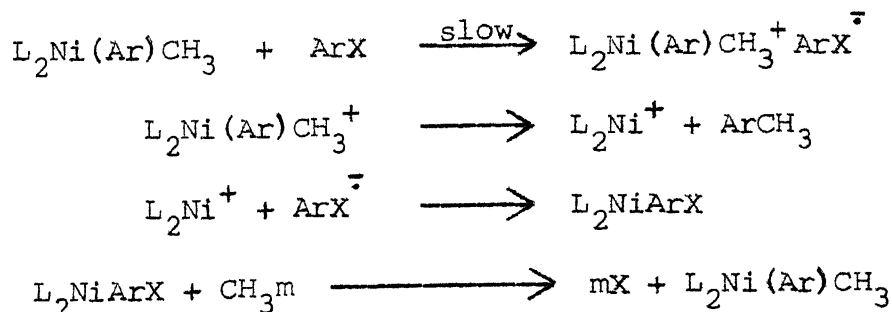
The second step has the earmarks of a displacement process, being fastest with primary and slower with secondary and tertiary-alkyl halides. Indeed, the latter are so slow that the competing decomposition of alkyl copper(I) species becomes the major reaction. Catalytic disproportionation proceeds by a homolytic mechanism^{38,48} in which copper(0) plays a role similar to that by iron as shown in Schemes V.4 and V.5. Vinylic iodides also undergo nucleophilic substitution at carbon with various Grignard reagents in the presence of catalytic amounts of copper salts.⁵⁰ The reaction occurs with retention of configuration.

The selective coupling of Grignard reagents with vinyl or aryl halides is also catalysed by various nickel complexes^{49,51-53} (Eq. 9):



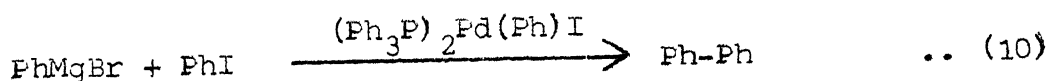
Since a variety of organonickel complexes are known, the mechanism of nickel catalysis is amenable to greater scrutiny than the iron system. The mechanism⁵⁴ proposed for such reactions is outlined in Scheme V.8:

SCHEME V.8



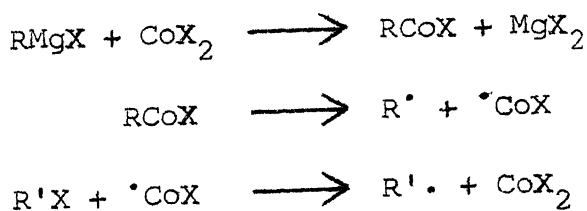
where, $L = PPh_3$ and $m = MgX$ or Li . It is likely that the reactions outlined in first three equations occur in one or two steps or in rapid succession before any of the intermediates diffuse apart. Such a simultaneous oxidation and transfer of an aryl group is difficult to distinguish from a stepwise process. However, the retention of stereochemistry at the vinylic centres in cis- and trans- β -bromostyrenes during cross coupling with phenyl magnesium bromide⁵⁵ indicates that organic free radicals do not intervene in these reactions.

The cross-coupling of aryl halides with Grignard reagents catalysed by Pd complexes⁵⁶ gave a variety of biaryls and alkylbenzenes (Eq. 10):

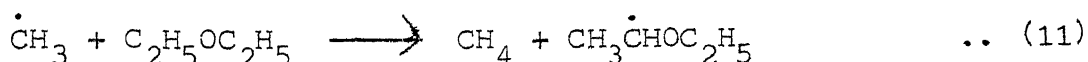


Cobalt compounds have also been employed as catalysts in the coupling of Grignard reagents with organic halides. These reactions are more commonly known as Kharasch reactions. Kharasch himself suggested^{3,57} that cobaltous subhalide was the actual catalytic species and that equimolar quantities of the Grignard reagent and the halide decomposed to free radicals (Scheme V.9):

SCHEME V.9



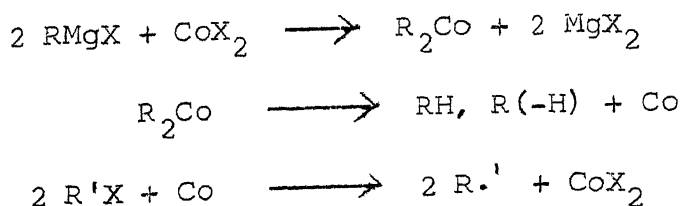
Norman and Waters⁵⁸ provided supporting evidence for the above steps based on the formation of a derivative of anthracene resulting from the attack by the radical $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$ in the reaction of methyl magnesium iodide with iodomethane in presence of cobaltous chloride and anthracene. The radical is supposed to have been formed according to Eq. (11):



However, Kharasch and Urry⁵⁹ had already raised doubts on the application of simple hydrogen abstraction step shown in Eq. (11). They observed that whereas free propyl radicals in solvent ether mainly abstracted hydrogen from the solvent to give propane, Kharasch reactions of propyl magnesium chloride with various alkyl halides yielded almost equal amounts of propane and propene, Kharasch and Urry⁵⁹ therefore, suggested that the propane and propene arose from a free radical/Grignard reagent/ether complex and that the free radicals in the complex could disproportionate more readily than free radicals in solution could.

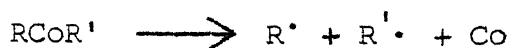
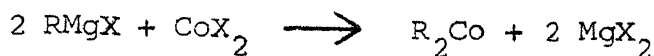
Wilds and McCormack⁶⁰ suggested that the cobalt metal was the active catalyst which attacked the organic halide $\text{R}'\text{X}$ (anethole hydromide) as shown in Scheme V.10:

SCHEME V.10

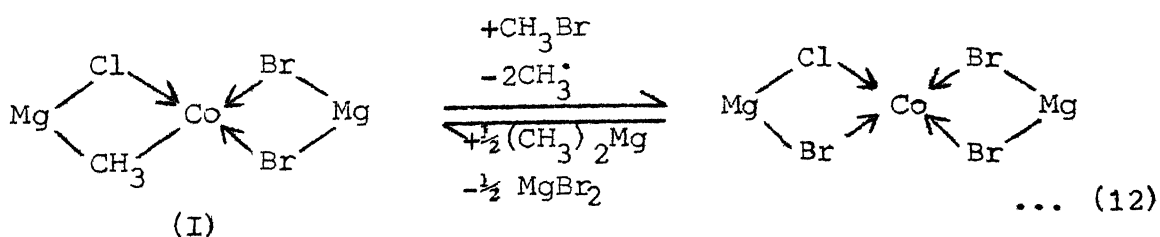


Later, Frey⁶¹ suggested a scheme in which both the Grignard reagent and the organic halide were necessary for the cobalt metal to react (Scheme V.11):

SCHEME V.11



Tsutsui⁶² proposed the formation of diphenyl cobalt intermediate that decomposed in a " π -radical hybridisation step" to give diphenyl in the catalysed reactions of phenyl magnesium bromide. Parker and Noller⁶³ reported that only a part of the products were derived from free radicals and the remaining products were formed by a non-free radical mechanism. They suggested that a catalyst complex, involving both alkyl halide and Grignard reagent, was formed and subsequently decomposed to give alkane from the alkyl halide and alkene from the Grignard reagent. Costa and coworkers⁶⁴ also suggested that a catalyst complex (I) was formed which reacted with alkyl halide, liberating free-radicals (Eq. 12):

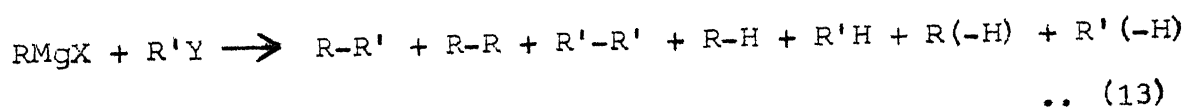


Costa and coworkers did not discuss the reactions of these radicals, but suggested⁶⁴ that this aspect of the Kharasch reaction merited further study.

It is evident from the above discussion that there is no general agreement as to the nature of the reactive catalyst and the mechanism involved in the Kharasch reaction. We, therefore, decided to study in some detail, the mechanism of homo-coupling and cross-coupling in some reactions of Grignard reagents with benzylic halides in the presence of cobalt catalysts.

V.3 Results and Discussion

A large number of reactions of Grignard reagents (RMgX) with organic halides (R'Y) in the absence of any metal catalysts are known⁶⁵ to give products attributable to free radical intermediates (Eq. 13):



Intermediacy of radicals is evident from our results on the reactions of two Grignard reagents namely, benzyl magnesium chloride and phenyl magnesium bromide with organic halide viz. benzyl chloride, benzhydryl chloride, trityl chloride, 9-bromofluorene and bromobenzene (Table V.1) wherein not only the homo-coupling and cross-coupling products are obtained but also the presence of radical species is indicated by ESR signals in

appropriately designed experiments.

Table V.1. Reaction of Grignard reagents, RMgX (0.01 mol) with organic halides, R'Y (0.01 mol) in THF for 3 hr.

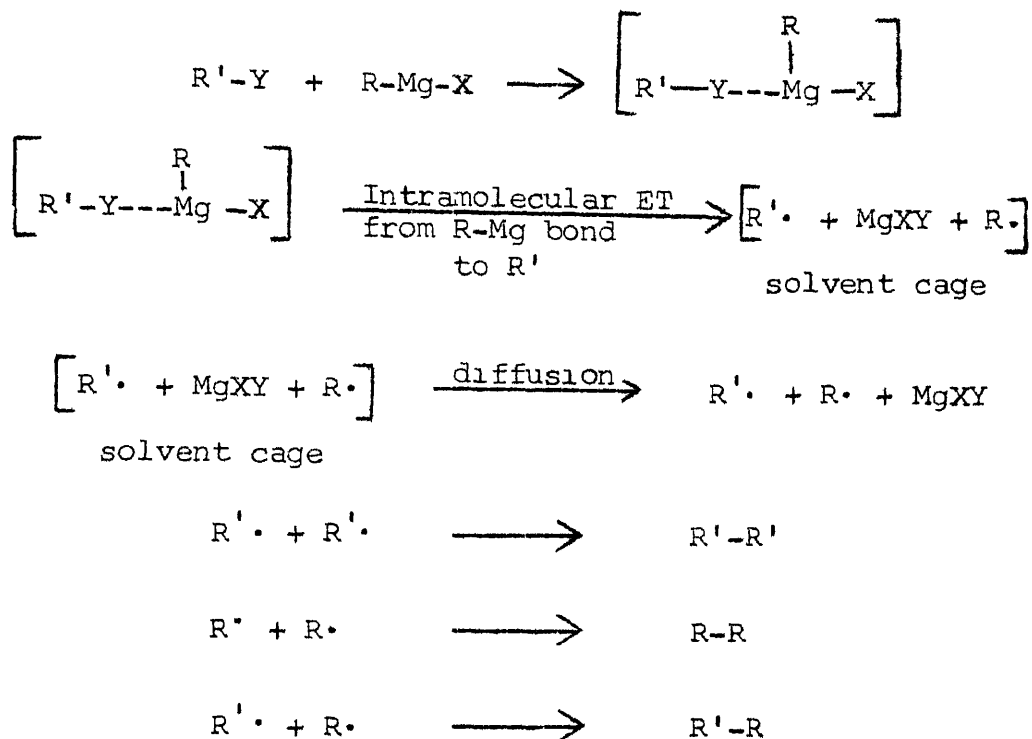
Run	RMgX	R'Y	% Yield of products ^{a,b}		
			R-R'	R-R ^c	R'-R'
1	PhCH ₂ MgCl	9-Bromofluorene	38	47	44
2	PhCH ₂ MgCl	Benzhydryl chloride	37	48	32
3	PhCH ₂ MgCl	Trityl chloride	44	48	27
4	PhCH ₂ MgCl	Bromobenzene	28	46	4
5	PhMgBr	Benzyl chloride	41	4	33
6	PhMgBr	9-Bromofluorene	35	7	43
7	PhMgBr	Benzhydryl chloride	45	6	36
8	PhMgBr	Trityl chloride	46	8	35

a, Yields of R-R' and R'-R' are based on the organic halide and those of R-R on the Grignard reagents.

b, In runs 4 through 8, substantial quantities of benzene were detected among the products but the yields were not determined.

c, Yields of the products R-R are recorded in this table after introducing correction for the amounts of these compounds formed during the preparation of the Grignard reagents.

Based on chemical and ESR evidence as well as the catalytic effect of light on these reactions, Singh and coworkers³³ have demonstrated the occurrence of an electron transfer free radical mechanism outlined in Scheme V.12.

SCHEME V.12

It is known that the reactions of Grignard reagents with organic halides when conducted in the presence of catalytic amounts of cobaltous halides result in the enhanced yields of the homo-coupling products $\text{R}'\text{-R}'$ and R-R at the expense of the cross-coupling products.⁶⁶ In order to examine the mechanistic aspects of these types of cobalt catalysed reactions, we carried out reactions of benzyl magnesium chloride with 9-bromofluorene and bromobenzene taken in equimolar quantities separately in the presence of 10 mole per cent of $\text{Co}^{\text{II}}\text{Cl}_2$. Similarly, the reaction between equimolar quantities of benzyl magnesium chloride and bromobenzene was also examined in the presence of 10 mole per cent of $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$. The results

are summarized in Table V.2.

Table V.2. Reaction of Grignard reagents, RMgX (0.01 mol) with organic halides, R'Y (0.01 mol) in the presence of cobalt compounds (0.001 mol) in THF for 3 hr.

Run	Cobalt compound	RMgX	R'Y	% Yield of products ^d			
				R-R'	R-R ^e	R'-R'	R'Y ^f
9	Co ^{II} Cl ₂	PhCH ₂ MgCl	9-Bromo-fluorene	5	45	32	49
10 ^g	Co ^{II} Cl ₂	PhCH ₂ MgCl	Bromo-benzene	3	43	24	50
11 ^{g,h}	(Co ^{III} en ₂ Cl ₂)Cl	PhCH ₂ MgCl	Bromo-benzene	3	48	25	54

d, Yields of R-R' and R'-R' are based on the organic halide and those of R-R on the Grignard reagents.

e, Yields of the products R-R are recorded in this table after introducing correction for the amounts of this compound formed during the preparation of the Grignard reagent.

f, Refers to the unreacted starting organic halide.

g, Small amounts of benzene were also detected among the products in runs 10 and 11; but yields were not determined.

h, Symbol en in (Co^{III}en₂Cl₂)Cl refers to ethylenediamine.

The results of Table V.2 clearly indicate that the effect of both the Co(II) and Co(III) catalysts is to enhance the yields of the homo-coupling products at the expense of the cross-coupling product; but approximately half of the starting halide remains unreacted in each reaction conducted with equimolar quantities of the Grignard reagent and the organic halide. It is apparent that for complete consumption of the organic

halide in these reactions, atleast double the molar quantity of the Grignard reagent is required. In view of these observations, the organic halides (0.01 mol) were reacted with Grignard reagents (0.022 mol) in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$ (0.001 mol). The results of these experiments are summarized in Table V.3.

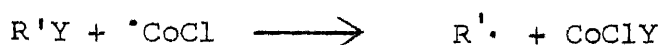
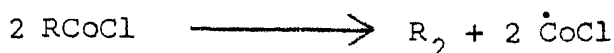
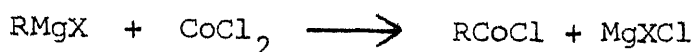
Table V.3. Reaction of Grignard reagents, RMgX (0.022 mol) with organic halides, $\text{R}'\text{Y}$ (0.01 mol) in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$ (0.001 mol) in THF for 3 hr.

Run	RMgX	R'Y	% Yield of products ^{i,j}		
			R-R'	R-R ^k	R'-R'
12	PhCH_2MgCl	9-Bromofluorene	7	86	68
13	PhCH_2MgCl	Benzhydryl chloride	8	81	56
14	PhCH_2MgCl	Trityl chloride	11	84	69
15	PhCH_2MgCl	Bromobenzene	4	86	45
16	PhMgBr	Benzyl chloride	5	29	55
17	PhMgBr	9-Bromofluorene	4	30	69
18	PhMgBr	Benzhydryl chloride	3	27	70
19	PhMgBr	Trityl chloride	4	24	73

- i, Yields of R-R' and R'-R' are based on the organic halide and those of R-R on the Grignard reagents.
- j, In runs 15 through 19, substantial quantities of benzene were detected among the products but the yields were not determined.
- k, Yields of the products R-R are recorded in this table after introducing correction for the amounts of these compounds formed during the preparation of the Grignard reagents.

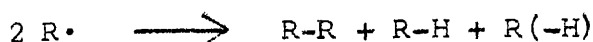
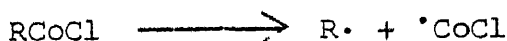
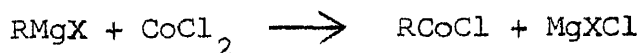
Preferential formation of homo-coupling products was earlier rationalized by Kharasch and Fields⁵⁷ in terms of the steps outlined in Scheme V.13:

SCHEME V.13

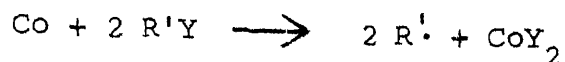
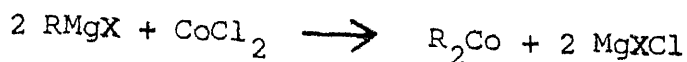


This mechanism involving the intervention of a cobalt subhalide (RCoCl) was further elaborated later by Kharasch and coworkers.⁶⁷ The mechanistic steps proposed by them are summarised in Scheme V.14:

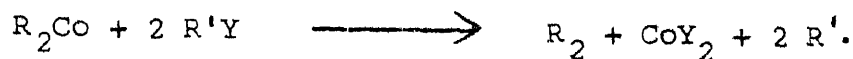
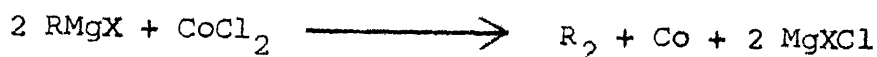
SCHEME V.14



In the meantime, Wilds and McCormack⁶⁰ proposed a mechanism which involved the intermediacy of metallic cobalt as active species. The steps of this mechanism are outlined in Scheme V.15:

SCHEME V.15

Another mechanism proposed by Davies, Hey and Tiecco⁶⁸ also involves metallic cobalt as the active species as shown in Scheme V.16:

SCHEME V.16

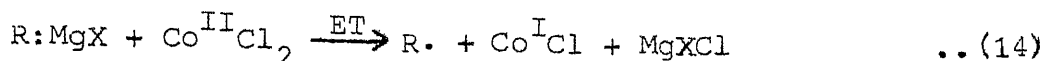
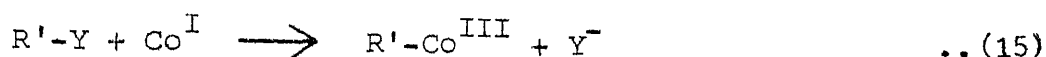
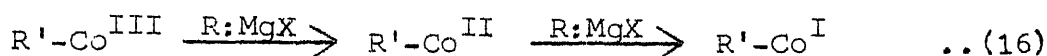
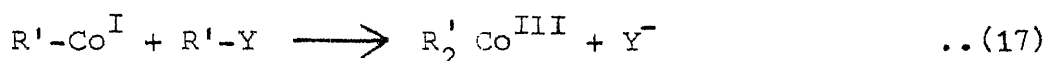
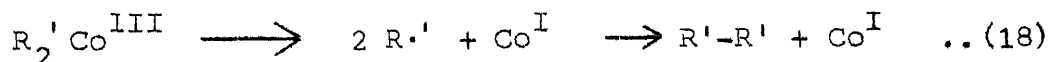
It is noteworthy that out of the four preceding mechanistic schemes, only one in Scheme V.16 accounts for the requirement of double the molar quantity of the Grignard reagent as compared to the organic halide. Davies, Done and Hey⁶⁹ have, however, suggested that evidence collected by them points to the metal derived from the catalyst as the 'active catalyst' rather than a metallic sub-halide or organometallic species.

In order to test the reactivity of metallic cobalt, Smith⁷⁰ prepared 'active cobalt' by reduction of cobaltous chloride with sodium naphthalene and found that it did not

react with ethyl bromide. This was confirmed by Frey,⁶¹ who also observed that addition of a Grignard reagent to cobaltous chloride in THF, produced metallic cobalt in a dark brown, finely-divided state. He showed that similar solutions, prepared by the reduction of $\text{Co}^{\text{II}}\text{Cl}_2$ with sodium naphthalene in THF would react with an organic halide only in the presence of Grignard reagent.

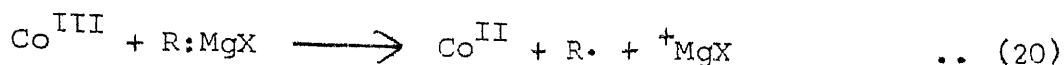
While the mechanism outlined in Scheme V.16 seems attractive on the basis of above arguments, its occurrence becomes doubtful as we could not detect the formation of metallic magnesium as suggested in it. An important point that has been missed by the earlier workers in this connection is the possibility of formation of $\text{Co}(\text{I})$ species by the reduction of CoCl_2 with the Grignard reagent. Cobalt(I) species are known to have high nucleophilicity and their extreme reactivity has prompted Schrauzer to coin the term, supernucleophile.⁷¹

We suggest that cobalt catalysis resulting in the enhanced yields of the homo-coupling products at the expense of the cross-coupling products in the reactions of Grignard reagents with organic halides may involve $\text{Co}(\text{I})$ as the active catalyst. A chain mechanism which accounts for the observed facts and involves $\text{Co}(\text{I})$ species as the chain carrier in the reactions catalyzed by CoCl_2 is outlined in Scheme V.17.

SCHEME V.17Electron transfer reduction of Co(II) by Grignard reagentNucleophilic attack by Co^I on the organic halideReduction of R'-Co^{III} by Grignard reagent to R'-Co^INucleophilic attack by R'-Co^I on the organic halideRegeneration of Co^I by thermal decomposition of R₂'Co^{III}Coupling of radicals R• derived from oxidation of Grignard reagent

After the initiation step (14), the steps (15) through (18) constitute a chain. Nucleophilic action of Co^I as in step (15) is preceded.⁷² In the event of this mechanisms being operative, Co^{III} compounds should like Co^{II} compounds, catalyse the

reaction with only one extra step prior to step (14) as shown in Eq. (20):



Our results relating to Co^{III} catalysis in the reactions of Grignard reagents with organic halides as listed in Table V.4 are in accordance with this view.

Table V.4. Reaction of Grignard reagents, RMgX (0.022 mol) with organic halides, $\text{R}'\text{Y}$ (0.01 mol) in the presence of $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$ (0.001 mol) in THF for 3 hr.

Run	RMgX	R'Y	% Yields of products ¹		
			R-R'	R-R ^m	R'-R'
20	PhCH_2MgCl	9-Bromofluorene	8	90	67
21	PhCH_2MgCl	Bromobenzene	3	84	46
22 ⁿ	PhMgBr	9-Bromofluorene	2	32	70

- 1, Yields of R-R' and R'-R' are based on the organic halide and those of R-R on the Grignard reagents.
- m, Yields of the products R-R are recorded in this table after introducing correction for the amounts of these compounds formed during the preparation of the Grignard reagents.
- n, In runs 21 & 22, substantial quantity of benzene was also detected among the products but the yield was not determined.

Oxidation of Grignard reagents by $\text{Co}^{\text{II}}\text{Cl}_2$ as in the initiation step (14) and by Co^{III} species as in step (16) has been found to occur in our experiments listed in Table V.5.

Table V.5. Reactions of cobalt compounds (0.01 mol) with only organic halide (0.01 mol) or only Grignard reagents (0.01 mol) in THF for 3 hr.

Run	Cobalt compound	Other reactant	Dimeric product (% yield)
23	$\text{Co}^{\text{II}}\text{Cl}_2$	PhCH_2Cl	$\text{PhCH}_2\text{-CH}_2\text{Ph}$ (18%)
24 ^p	$\text{Co}^{\text{II}}\text{Cl}_2$	PhCH_2MgCl	$\text{PhCH}_2\text{-CH}_2\text{Ph}$ (14%)
25 ^{p,q}	$(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$	PhCH_2MgCl	$\text{PhCH}_2\text{-CH}_2\text{Ph}$ (58%)

p. 1) Yields of the dimeric products are recorded in this table after introducing correction for the amounts of these compounds formed during the preparation of the Grignard reagents.

1) In the presence of α -methylstyrene (0.15 mol) runs 24 and 25 gave lower yields of dimeric products and a polymeric product was produced in each case.

q. Symbol en in $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$ refers to ethylenediamine.

Formation of radical intermediates corresponding to the alkyl group of the Grignard reagents is indicated by the experiments of runs 24 and 25 in the presence of α -methylstyrene, which produced a polymeric substance at the expense of the dimeric products. Production of radicals derived from organic halides in their reactions with Grignard reagents in the presence of cobalt catalysts is already documented.⁷³ Step (15) in the case of bromobenzene might occur either by oxidative addition⁷² with the supernucleophile Co^{I} behaving as an unusually powerful nucleophile for the aryl halide or by a path similar to that

suggested in the literature⁷⁴ for the formation of Ph_2NiI_2 from iodobenzene and a nickel complex. The organocobalt compounds visualized as intermediates in Scheme V.17 must be highly reactive, transient species making it unlikely to detect them directly.⁶⁹

In conclusion, we suggest that while uncatalysed reactions between Grignard reagents and organic halides yield cross-coupling and homo-coupling products by an electron transfer radical process outlined in Scheme V.12, a major part of the reaction when catalysed by Co^{II} or Co^{III} species occurs by a chain process initiated by the electron transfer reduction of cobalt compound with the Grignard reagent, wherein Co^{I} may act as the active catalyst (Scheme V.17). A distinction between this new suggestion and the earlier suggestions where metallic cobalt is proposed to be the active catalyst is not possible at this stage.

V.4 Experimental

All the melting points were taken on MEL-TEMP melting point apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer models-137 and 580 spectrophotometers. ESR spectra were recorded on Varian model V-4502 EPR spectrometer system operating at X-band with 10 KC modulation. Compounds were characterized by comparison of their IR spectra with those of the authentic samples, melting points, TLC and mixed

melting point techniques. GLC analyses were carried out using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Literature melting points are cited from "Handbook of Chemistry and Physics," 50th edition, R.C. Weast (Ed.), published by the Chemical Rubber Company, Cleaveland, Ohio, unless otherwise specified. Silica-gel (asc-India) was used for TLC analyses. THF was purified by the same method as described in Chapter II.

Starting Materials

Benzyl chloride (E. Merck) and bromobenzene (SDS) were used after distillation. Magnesium metal (BDH, Poole, Englad, Grignard Grade) was used after cleaning with methanol followed by ether and then drying in an oven at 60°C for 1 hr. 9-Bromo-fluorene, benzhydryl chloride and trityl chloride were prepared by known procedures (ref. cited in previous chapters). CoCl_2 (BDH, Analar) was used and $[\text{Co}(\text{en}_2\text{Cl}_2)] \text{Cl}^{75}$ where, $\text{en} = \text{H}_2\text{NCH}_2\text{-CH}_2\text{NH}_2$ was prepared by the known method.

Preparation of Grignard Reagents: Benzyl magnesium chloride and Phenyl magnesium bromide

Benzyl magnesium chloride and phenyl magnesium bromide were prepared by standard procedures. In general, a perfectly dry 3-necked 250 ml RB flask was mounted on a magnetic stirring base, fitted with a condenser, a gas passing adaptor and a dropping funnel. Benzyl chloride (0.0125 mol or 0.028 mol) and bromobenzene (0.011 mol or 0.023 mol) were used during Grignard reagent preparation. Magnesium metal (10-15% in

excess of the stoichiometric amount) was placed in the flask and covered with dry THF (25 ml for the smaller quantity of the halide and 50 ml for the higher quantity of the halide). A crystal of iodine was added and the reaction was started by slow addition of the organic halide dissolved in dry THF (25 ml for the smaller quantity of the halide and 50 ml for the higher quantity of the halide). The addition of organic halide was regulated such that the reaction proceeded at a moderate rate with gentle refluxing. After 2-3 hr the reaction mixture was poured into water and products extracted with ether. GLC analyses of the product mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of bibenzyl ($\sim 20\%$) in the reactions of benzyl magnesium chloride and biphenyl ($\sim 5\%$) in the reactions of bromobenzene, by calibration method.

Reaction of Benzyl magnesium chloride with 9-Bromofluorene

A solution of 9-bromofluorene (2.45 g, 0.01 mol) in dry THF (50 ml) was placed in a 250 ml RB flask mounted over a magnetic stirring base, under N_2 atmosphere. Benzyl magnesium chloride solution (50 ml) prepared from benzyl chloride (1.58 g, 0.0125 mol) was added to the flask under N_2 atmosphere. The mixture was refluxed for 3 hrs and the contents of the flask then cooled to room temperature. The reaction mixture was worked up after addition to acidified water. The products were extracted with ether and the ethereal extract dried over

MgSO₄ (anhyd.). Column chromatography of the crude mixture on an activated silica-gel column using petroleum ether (b.p. 60-80°), petroleum ether (b.p. 60-80°)-benzene (50:50 v/v) and benzene as eluants gave bibenzyl 0.656 g, 9-benzylfluorene (0.973 g, ~38%) and 9,9'-bifluorenyl (0.725 g, ~44%). The effective yield of bibenzyl excluding its formation during the Grignard reagent preparation was 0.656 - 0.225 = 0.431 g (~47%). The compounds were characterized by mixed m.p. technique and comparison of IR spectra with those of authentic samples.

Reaction of Benzyl magnesium chloride with Benzhydryl chloride

To a solution of benzhydryl chloride (2.02 g, 0.01 mol) in 50 ml of dry THF was added a solution of benzyl magnesium chloride (50 ml) prepared from benzyl chloride (1.58 g, 0.0125 mol) under N₂ atmosphere. The reaction was carried out by refluxing the mixture for 3 hr after which the mixture was cooled to room temperature. The reaction mixture was worked up after addition to acidified water and the products extracted with solvent ether. Separation of products on an activated silica-gel column using petroleum ether (b.p. 60-80°), petroleum ether (60-80°)-benzene (50:50 v/v) and benzene as eluants yielded bibenzyl (0.665 g), 1,1,2-triphenylethane (0.95 g, ~37%) and 1,1,2,2-tetraphenylethane (0.53 g, ~32%). The effective yield of bibenzyl in this reaction was 0.665 - 0.227 = 0.438 g (~48%). The compounds were characterized by melting point, mixed m.p. technique and comparison of their IR spectra with those of the authentic samples.

Reaction of Benzyl magnesium chloride with Trityl chloride

To a solution of trityl chloride (2.78 g, 0.01 mol) in dry THF (50 ml) was added a solution of benzyl magnesium chloride prepared from benzyl chloride (1.58 g, 0.0125 mol) in dry THF (50 ml) under N_2 atmosphere. A reddish-brown color appeared instantaneously which darkened on complete addition. The color faded to dull yellow with time. The reaction mixture was worked up and products extracted as usual. From the dried ($MgSO_4$) ethereal extract the solvent was removed. The crude mixture of products was chromatographed over silica-gel column using petroleum ether (b.p. 60-80°), petroleum ether-benzene, (50:50 v/v) and benzene as eluants. Products obtained in this manner were bibenzyl (0.66 g), 1,1,1,2-tetraphenylethane (1.46 g, 44%) and hexaphenylethane (1.31 g, 27%). The effective yield of bibenzyl, therefore, was $0.66 - 0.237 = 0.423$ g (48%). The products were identified by m.p., mixed m.p. technique and comparison of their IR spectra with those of the authentic samples. When this reaction was repeated in the cavity of ESR spectrometer, ESR signals were observed. The signals were not observed with pure reactants.

Reaction of Benzyl magnesium chloride with Bromobenzene

To a solution of bromobenzene (1.57 g, 0.01 mol) in 50 ml of dry THF was added a solution of benzyl magnesium chloride in dry THF (50 ml) prepared from benzyl chloride (1.58 g, 0.0125 mol) under N_2 atmosphere. The mixture was gently refluxed for

3 hr and then worked up as usual. TLC analyses of the concentrated, dried ethereal extract showed spots corresponding to biphenyl, diphenylmethane and bibenzyl. GLC analysis of the reaction mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of diphenylmethane ~28%, biphenyl ~4% and bibenzyl ~46% (excluding the amount formed during Grignard reagent preparation) by calibration method. Benzene was also detected among the products by GLC.

Reaction of Phenyl magnesium bromide with Benzyl chloride

A solution of benzyl chloride (1.27 g, 0.01 mol) in 50 ml of dry THF was placed in a 3-necked flask mounted over a magnetic stirring base under N_2 atmosphere. To it was added phenyl magnesium bromide solution (50 ml) prepared from bromobenzene (1.73 g, 0.011 mol) under N_2 atmosphere and the mixture gently refluxed for 3 hr. The contents of the flask were then cooled and added to acidified water. The products were extracted with ether, the ethereal extract washed with water and dried over anhydrous $MgSO_4$. Solvent ether was removed at about 40°C. TLC analyses of the crude mixture of products showed spots corresponding to biphenyl, diphenylmethane and bibenzyl. GLC analysis of the mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the presence of biphenyl ~4% (excluding the amount formed during the Grignard reagent preparation), diphenylmethane ~41% and bibenzyl ~33% by calibration method. Besides these products, a peak corresponding to benzene was also observed.

Reaction of Phenyl magnesium bromide with 9-Bromofluorene

To a solution of 9-bromofluorene (2.45 g, 0.01 mol) in THF (50 ml) kept under pure and dry nitrogen, was added a solution (50 ml) of phenyl magnesium bromide prepared from 1.73 g of bromobenzene (0.011 mol). The mixture was refluxed gently and worked up as in the above experiments. The products were extracted with ether, the extract washed with water and dried over anhydrous MgSO_4 . GLC analysis indicated the presence of benzene in the ethereal extract. Column chromatography of the crude product mixture over activated silica-gel column using petroleum ether (b.p. 60-80°) and petroleum ether-benzene (50:50 v/v) as eluants gave biphenyl 0.098 g, the effective yield being $0.098 - 0.042 = 0.056$ g (~7%), fluorene (0.065 g, ~4%), 9-phenylfluorene (0.84 g, ~35%) and 9,9'-bi-fluorenyl (0.70 g, ~43%). The products were characterized by m.p., mixed m.p. technique, TLC and comparison of their IR spectra with those of the authentic samples.

Reaction of Phenyl magnesium bromide with Benzhydryl chloride

To a solution of benzhydryl chloride (2.02 g, 0.01 mol) in THF (50 ml) was added a solution of phenyl magnesium bromide in 50 ml of THF prepared from bromobenzene (1.73 g, 0.011 mol) under an atmosphere of N_2 . The reaction mixture was refluxed gently for a period of 3 hr after which it was cooled to room temperature and worked up after addition to acidified water. Extraction of products with solvent ether followed by washing.

of the extract with water and drying over MgSO_4 (anhyd.) yielded a crude product mixture, the GLC analyses of which indicated the formation of benzene. The concentrated crude mixture of products was subjected to column chromatography over an activated silica-gel column using petroleum ether (b.p. 60-80°) and petroleum ether (b.p. 60-80°)-benzene (50:50 v/v) as eluants. The products obtained were biphenyl 0.090 g, the effective yield due to the reaction being $0.090 - 0.042 = 0.048$, (~6%, triphenylmethane (1.09 g, ~45%) and 1,1,2,2-tetraphenylethane (0.60 g, ~36%). The compounds were characterized by m.p., mixed m.p. technique and comparison of their IR spectra with those of the authentic samples.

Reaction of Phenyl magnesium bromide with Trityl chloride

To a solution of trityl chloride (2.78 g, 0.01 mol) in dry THF (50 ml) was added phenyl magnesium bromide solution (50 ml) prepared from bromobenzene (1.74 g, 0.011 mol) under conditions identical to those mentioned in the above experiment. A tan color was produced instantaneously which changed to cherry-red after 30 min. The color became dull with time and stayed yellow after an hour. Reaction was worked up in the usual manner. The product mixture obtained after concentrating the ethereal extract indicated the formation of benzene and biphenyl, 0.105 g, the net yield of biphenyl, therefore, being $0.105 - 0.042 = 0.063$, (~8%) on GLC analysis using 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The product mixture

was then subjected to column chromatography using petroleum ether (b.p. 60- 80°), petroleum ether (b.p. 60-80°)-benzene (50:50 v/v) and benzene as eluants. The products obtained were tetraphenylmethane (1.47 g, ~46%) and hexaphenylethane (0.85 g, ~35%). The products were identified by m.p., mixed m.p. technique and C, H analyses.

Reaction of Benzyl magnesium chloride with 9-Bromofluorene in presence of $\text{Co}^{\text{II}}\text{Cl}_2$

In a 250 ml 3-necked flask, mounted over a magnetic stirring base, was placed 9-bromofluorene (2.45 g, 0.01 mol) and $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) in 50 ml of dry THF. To this was added a solution of benzyl magnesium chloride in THF (50 ml) prepared from benzyl chloride (1.58 g, 0.0125 mol) under N_2 atmosphere. The reaction mixture was refluxed for a period of 3 hr after which it was cooled to room temperature and worked-up after addition to acidified water. The products were extracted with ether, the ethereal extract washed with water and dried over MgSO_4 (anhyd.). The product mixture obtained after evaporation of the solvent was charged on an activated silica-gel column and the products separated using petroleum ether (b.p. 60-66°) and petroleum ether (b.p. 60-66°)-benzene (50:50, v/v) as eluants. The products obtained were bibenzyl (0.636 g), 9-bromofluorene (1.20 g, ~49%), 9-benzylfluorene (0.17 g, ~5%) and 9,9'-bifluorenyl (0.525 g, ~32%). The effective yield of bibenzyl due to the reaction was $0.638 - 0.227 = 0.411\text{g}$ (~45%).

$2.14 - 0.51 = 1.63$, (~81%), 1,1,2-triphenylethane (0.206 g, ~8%) and 1,1,2,2-tetraphenylethane (0.930 g, ~56%).

Reaction of Benzyl magnesium chloride with Trityl chloride in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

The reaction of trityl chloride (2.78 g, 0.01 mol) and $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) with benzyl magnesium chloride was carried out in the same way as the above experiments under identical conditions. Separation of products on a silica-gel column in the usual manner yielded bibenzyl 2.2 g (including 0.51 g formed in the preparation of Grignard reagent) the effective yield being $2.20 - 0.51 = 1.69$ g (~84%), 1,1,1,2-tetraphenylethane (0.36 g, ~11%) and hexaphenylethane (1.58 g, ~65%).

Reaction of Benzyl magnesium chloride with Bromobenzene in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

The reaction of bromobenzene (1.57 g, 0.01 mol) taken in THF (50 ml) with benzyl magnesium chloride solution (100 ml) prepared from benzyl chloride (3.54 g, 0.028 mol) in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) was carried out as the previous experiments. After extracting the products with ether and washing the ethereal extract with water, the ethereal extract was dried over MgSO_4 (anhyd.). The crude mixture of products obtained after concentration at about 40° was subjected to GLC analyses using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. The distribution of products in the

reaction mixture as indicated by calibration method was diphenylmethane (0.067 g, ~4%) biphenyl (0.346 g, ~45%) and bibenzyl 1.97 g. Accounting for 0.51 g of bibenzyl formed during the Grignard reagent preparation, the net yield of bibenzyl is $1.97 \text{ g} - 0.51 \text{ g} = 1.46 \text{ g}$ (~73%). Benzene was also detected by GLC but its yield was not determined.

Reaction of Phenyl magnesium bromide with Benzyl chloride in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

In a 3-necked flask, mounted over a magnetic stirring base were placed benzyl chloride (1.265 g, 0.01 mol), $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) and 50 ml of dry THF. A solution of phenyl magnesium bromide prepared from bromobenzene (3.611 g, 0.023 mol) in 100 ml of dry THF was added to it under N_2 atmosphere. The reaction mixture was refluxed for 3 hr, cooled to room temperature and then worked up after addition to acidified water. The products were extracted with ether, the ethereal extract washed with water and dried over MgSO_4 . The mixture of products obtained after concentration at about 40° was subjected to GLC analysis using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length. Besides benzene, the formation of diphenylmethane (0.141 g, ~5%), bibenzyl (0.50 g, ~55%) and biphenyl 0.57 g was noticed. Since 0.080 g of biphenyl was formed during Grignard reagent preparation, the effective yield of biphenyl is $0.570 - 0.080 = 0.490 \text{ g}$ (~29%).

Reaction of Phenyl magnesium bromide with 9-Bromofluorene in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

The above reaction was repeated using 9-bromofluorene (2.45 g, 0.01 mol) in place of benzyl chloride under otherwise identical reaction conditions. Separation of products on a silica-gel column as usual yielded biphenyl 0.590 g, 9-phenylfluorene (0.097 g, $\sim 4\%$) and 9,9'-bifluorenyl (1.138 g, $\sim 69\%$). The net yield of biphenyl due to the reaction was $0.590 - 0.080 = 0.510$ g ($\sim 30\%$). Formation of benzene in the reaction was also noticed by GLC as usual.

Reaction of Phenyl magnesium bromide with Benzhydryl chloride in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

The reaction between benzhydryl chloride (2.02 g, 0.01 mol), $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) and phenyl magnesium bromide prepared from bromobenzene (3.611 g, 0.023 mol) in a total of 150 ml of dry THF under N_2 atmosphere was carried out in the same manner as the above experiments. After work-up of the reaction mixture in the usual manner, the products were separated on an activated silica-gel column using petroleum ether (b.p. 60-80°) and petroleum ether (b.p. 60-80°)-benzene (50:50, v/v) as eluants. The products obtained were biphenyl 0.538 g, triphenylmethane (0.075 g, $\sim 3\%$) and 1,1,2,2-tetraphenylethane (1.165 g, $\sim 70\%$). Since 0.080 g of biphenyl is formed during preparation of the Grignard reagent, the net yield of biphenyl obtained was $0.538 - 0.080 = 0.458$ g ($\sim 27\%$). Formation of

benzene in the reaction was detected by GLC.

Reaction of Phenyl magnesium bromide with Trityl chloride in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

The above reaction was repeated using trityl chloride (2.78 g, 0.01 mol) in place of benzhydryl chloride under otherwise identical conditions. Separation of products in the usual manner yielded biphenyl 0.49 g, tetraphenylmethane (0.125 g, ~4%) and hexaphenylethane (1.77 g, ~73%). The yield of biphenyl after correcting for its formation during the Grignard reagent preparation is $0.490 - 0.080 = 0.410$ g (~24%). Benzene was detected among the products of the reaction by GLC method.

Reaction of Benzyl magnesium chloride with 9-Bromofluorene in the presence of Co^{III} complex

In a 250 ml 3-necked flask, mounted over a magnetic stirring base were placed 9-bromofluorene (2.45 g, 0.01 mol), $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$ (0.286 g, 0.001 mol) and dry THF (50 ml). A solution of benzyl magnesium chloride prepared from (3.54 g, 0.028 mol) of benzyl chloride in 100 ml of dry THF was added to the 3-necked flask under N_2 atmosphere. The reaction mixture was refluxed for a period of 3 hr after which it was cooled to room temperature and worked up as usual. Separation of products on a silica-gel column yielded bibenzyl 2.31 g, 9-benzylfluorene (0.20 g, ~8%) and 9,9'-bifluorenyl (1.10 g, ~67%). The net yield of bibenzyl due to the reaction is

$2.31 - 0.51 = 1.80 \text{ g } (\sim 90\%)$.

Reaction of Benzyl magnesium chloride with Bromobenzene in the presence of Co^{III} complex

The above reaction was repeated using bromobenzene (1.57 g, 0.01 mol) in place of 9-bromofluorene. The reaction mixture was worked up after addition to acidified water. The products were extracted with ether, the ethereal extract washed with water and dried over MgSO_4 . The GLC analyses of the product mixture obtained after concentration of the ethereal extract at about 40° , using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the formation of benzene, diphenylmethane (0.050 g, $\sim 3\%$), biphenyl (0.354 g, $\sim 46\%$) and bibenzyl 2.19 g. The net yield of bibenzyl due to the reaction with the halide is $2.19 - 0.51 = 1.68\text{g} (\sim 84\%)$.

Reaction of Phenyl magnesium bromide with 9-Bromofluorene in the presence of Co^{III} complex

In a 250 ml 3-necked flask were placed 9-bromofluorene (2.45 g, 0.01 mol), $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$ (0.286 g, 0.001 mol) and dry THF (50 ml). To this was added a solution of phenylmagnesium bromide prepared from 3.611 g (0.023 mol) of bromobenzene in 100 ml of dry THF. The reaction was conducted in the manner described above. Separation of products on a silica-gel column using petroleum ether (b.p. $60-66^\circ$) and petroleum ether (b.p. $60-66^\circ$)-benzene (50:50, v/v) yielded 0.62 g of biphenyl, 0.050 g ($\sim 2\%$) of 9-phenylfluorene and 1.15 g ($\sim 70\%$)

of 9,9'-bifluorenyl. The effective yield of biphenyl in the reaction was $0.62 - 0.080 = 0.54$ g ($\sim 32\%$). Formation of benzene in the reaction was detected by GLC method.

Reaction of CoCl_2 with Benzyl chloride

To a solution of benzyl chloride (1.265 g, 0.01 mol) in dry THF (50 ml) kept under nitrogen atmosphere, was added $\text{Co}^{\text{II}}\text{Cl}_2$ (1.30 g, 0.01 mol). The mixture was refluxed for 3 hr, then cooled to room temperature and poured into acidified water. The mixture was extracted with ether, the ethereal extract washed with water and dried (MgSO_4). After removal of the solvent, the resultant mixture was subjected to GLC analysis using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length which indicated the presence of bibenzyl (0.164 g, $\sim 18\%$) and benzyl chloride (1.01 g, $\sim 80\%$).

Reaction of Benzyl magnesium chloride with $\text{Co}^{\text{II}}\text{Cl}_2$

To a 250 ml 3-necked flask containing benzyl magnesium chloride prepared from benzyl chloride (1.58 g, 0.0125 mol) in THF (50 ml) kept under N_2 atmosphere was added $\text{Co}^{\text{II}}\text{Cl}_2$ (1.30 g, 0.01 mol). A dark color appeared immediately on the addition of $\text{Co}^{\text{II}}\text{Cl}_2$. The reaction mixture was refluxed for 3 hr and then worked up as usual. GLC analysis of the crude product using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the formation of bibenzyl (0.387 g, $\sim 34\%$) by calibration method. This includes $\sim 20\%$ bibenzyl formed

during the Grignard reagent preparation, so the effective yield of bibenzyl was ~14%.

Repetition of the above experiment in the presence of α -methylstyrene (17.7 g, 0.15 mol) resulted in the formation of a polymeric material along with bibenzyl. On comparison with the above reaction by TLC showed the formation of bibenzyl in diminished yield.

Reaction of Benzyl magnesium chloride with $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$

The reaction of benzyl magnesium chloride prepared from benzyl chloride (1.58 g, 0.125 mol) in THF (50 ml) was conducted with $(\text{Co}^{\text{III}}\text{en}_2\text{Cl}_2)\text{Cl}$ (2.86 g, 0.01 mol) under dry nitrogen atmosphere for 3 hr and then worked up after addition to acidified water. The mixture was extracted with ether, the ethereal extract washed with water and dried over MgSO_4 (anhyd.) GLC analysis of the concentrated product mixture using a 10% SE-30 on Crom-P (85-100 M) column of 2 m length indicated the formation of 0.71 g (~78%) of bibenzyl including ~20% of bibenzyl formed during the Grignard reagent preparation, so the effective yield of bibenzyl in this reaction is 58%.

Repetition of the above experiment in the presence of α -methylstyrene (17.7 g, 0.15 mol) resulted in the formation of a polymeric material along with bibenzyl. On comparison with the above reaction by TLC showed the formation of bibenzyl in diminished yield.

V.5 References

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CHAPTER VI

SUMMARY AND CONCLUSIONS

In this thesis, reactions of six different categories have been examined in some detail and new mechanistic interpretations offered in each case. Various categories of reactions are:

(i) reduction of benzylic halides with lithium aluminium hydride in THF medium at ice-bath temperature under nitrogen atmosphere,

(ii) reductive cyclization of Z-2-chlorostilbene to phenanthrene with lithium aluminium hydride in THF medium at room temperature under nitrogen atmosphere,

(iii) lithium aluminium hydride induced isomerization of Z-stilbene to E-stilbene in THF medium at room temperature under nitrogen atmosphere,

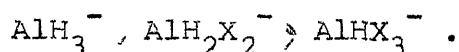
(iv) sodium dithionite reduction of benzylic halides in dimethylformamide medium at reflux temperature under nitrogen atmosphere,

(v) reduction and dimethylamination of benzylic halides in presence of cobaltous chloride or ferrous oxalate in dimethylformamide medium at reflux temperature under nitrogen atmosphere, and

(vi) catalysis by cobalt(II) and cobalt(III) species in the reactions of Grignard reagents with organic halides in THF medium at reflux temperature under nitrogen atmosphere.

In the reduction of 9-chloromethylantracene, benzhydryl chloride and 9-bromofluorene with lithium aluminium hydride, each benzylic halide, Ar-CH(R)-X , completely reacted with an equimolar amount of the reducing agent giving ArCH_2R and ArCH(R)-CH(R)Ar along with gaseous hydrogen. Use of one-half or one-fourth molar quantity of the reducing agent gave these same products in different proportions. Aluminium hydride, under the same conditions, does not reduce any of the halides. In the reactions of benzhydryl chloride and 9-bromofluorene with equimolar quantities of lithium aluminium hydride, distinct ESR signals were observed. These signals were not present in the pure reactants. A new mechanism has been established for these reactions in which AlH_4^- serves as electron donor towards the halides. The benzylic halides are thus transformed into the corresponding radical-anions which decompose to give benzylic radicals. AlH_4^- also serves as a source of hydrogen atom towards these radicals converting itself into the alane radical-anion AlH_3^- which, in turn, transfers its extra electron

to a fresh molecule of the halide in competition with AlH_4^- . Mixed hydrides - AlH_3X^- , AlH_2X_2^- and AlHX_3^- when produced in the medium serve the same two purposes as inferior alternatives to AlH_4^- with the efficiency decreasing in the order:



In the first example of a quantitative, uncatalysed lithium aluminium hydride reduction of an aryl chloride viz. Z-2-chlorostilbene, AlH_4^- is again found to act as an electron donor producing radical-anion of the aryl halide. Extended conjugation in the aryl halide provides ABMO of low enough energy to facilitate electron acceptance. The aryl halide radical-anion expels chloride anion producing an aryl radical with two phenyl rings situated on the same side of the central double bond. Intramolecular free radical aromatic substitution aided by a favorable distance of the order of 1.5 Å between the two positions to be linked ultimately produces phenanthrene in high yield.

Isomerization of Z-stilbene to E-stilbene was found to occur quantitatively in presence of a large excess (ten-fold excess) of lithium aluminium hydride. It is found that AlH_4^- initially transfers an electron to the Z-stilbene producing the hydrocarbon radical-anion which is formed in large amounts in presence of an excess of the reducing agent. The radical-anion subsequently disproportionates giving the hydrocarbon and its dianion. It is at the dianion stage that the bond order of the

central carbon-carbon bond is sufficiently reduced permitting rotation about the central bond. The dianion corresponding to E-stilbene formed in this way, loses two electrons to the surroundings giving E-stilbene.

In the sodium dithionite reduction of 4-nitrobenzyl bromide, 9-bromofluorene, benzhydryl chloride and 9-chloromethylantracene each halide, ArCH(R)-X gave a dimeric product, Ar-CH(R)-CH(R)-Ar in addition to sulfur dioxide gas. 4-Nitrobenzyl bromide, 9-bromofluorene and 9-chloromethylantracene also gave dehalogenation products, $\text{Ar-CH}_2\text{-R}$; but in the case of benzhydryl chloride, fluorene instead of diphenylmethane was obtained. Olefinic dimers, Ar-C(R)=C(R)-Ar were also obtained with the former two halides and perhaps with 9-chloromethylantracene. The sulfone, $4\text{-O}_2\text{N-C}_6\text{H}_4\text{-CH}_2\text{-SO}_2\text{-CH}_2\text{-C}_6\text{H}_4\text{-NO}_2$ was isolated among the products of the reaction of 4-nitrobenzyl bromide. As the dithionite anion exists largely in the form of sulfur dioxide radical-anion at the reflux temperature of DMF, a mechanism initiated by transfer of an electron from the sulfur dioxide radical-anion ($\text{SO}_2^{\cdot-}$) to the benzylic halide has been proposed. Benzylic radicals produced by the dissociation of benzylic halide radical-anions intervene effectively in the formation of the dimeric products, Ar-CH(R)-CH(R)-Ar and other processes. It is found that the sulfone is formed via coupling between the 4-nitrobenzyl radical and the sulfinic anion produced in the medium. Carbanions are found to intervene in the formation of the dehalogenation products, $\text{Ar-CH}_2\text{-R}$ as

well as the olefinic dimers, Ar-C(R)=C(R)-Ar . Benzhydryl radical undergoes intramolecular cyclization giving fluorene.

In the studies on the reduction and dimethylamination of five benzylic halides viz. benzyl chloride, 4-nitrobenzyl bromide, 9-bromofluorene, benzhydryl chloride and trityl chloride in the presence of cobaltous chloride or ferrous oxalate in DMF at reflux temperature, Co(II) is found to influence the course of all the reactions by acting as electron donor to the halides via outer sphere electron transfer process. Fe(II) also behaves similarly with 4-nitrobenzyl bromide; but preferentially forms an organoiron complex with other halides (excepting trityl chloride) via oxidative addition involving a 3-center, concerted, frontside nucleophilic displacement mechanism. The unstable organoiron complex undergoes a facile, concerted orbital symmetry allowed reaction giving dimeric products. Radicals do not intervene in the latter reactions. Product analysis, blank experiments in the absence of metal ions, and other control experiments indicate that under the conditions employed, DMF brings about nucleophilic displacement of halogen by $\text{S}_{\text{N}}2$ type attack on 4-nitrobenzyl bromide and $\text{S}_{\text{N}}1$ type attack on all other halides, through its oxygen atom. Dimethylamination takes place when DMF is oxidized by electron transfer process into the DMF radical-cation which couples through its nitrogen atom with benzylic radicals producing an intermediate leading to the benzylic dimethylamines. The mechanistic conclusions made here are tentative.

VITAE

Born on May 11, 1954 at Delhi, Jitender Mohan Khurana after having his early education from Government Higher Secondary School, Vijay Nagar, Delhi, joined Ramjas College, University of Delhi in July 1970. He received the degree of Bachelor of Science in Chemistry (Hons.) in 1973 and the degree of Master of Science in 1975 from University of Delhi, respectively. He joined the graduate programme in the Department of Chemistry, Indian Institute of Technology, Kanpur in July 1975. Presently he is a Senior Research Assistant in the Department of Chemistry.

Studies reported in this thesis have thus led to mechanistic delineation of some new electron transfer pathways involving lithium aluminium hydride, sodium dithionite, cobalt(II) and iron(II) species as electron donors. Logical mechanistic interpretations have also been offered towards rationalizing the roles of iron(II) species in the non-radical, reductive dimerization of alkyl halides; dimethylformamide in nucleophilic displacements and dimethylaminations; and cobalt(II) and cobalt(III) species in the reactions of Grignard reagents with organic halides which though speculative to some extent, should stimulate further interest towards a deeper and clearer understanding of related mechanisms in general and catalytic action by metal ions and complexes in particular.

the formation of diphenylmethane $\sim 30\%$ (0.050 g), bromobenzene $\sim 54\%$ (0.848 g), biphenyl $\sim 25\%$ (0.192%) and bibenzyl 0.665 g. Therefore, the effective yield of bibenzyl is $0.665 - 0.227 = 0.438$ g ($\sim 48\%$).

Reaction of Benzyl magnesium chloride with 9-Bromofluorene in the the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

In a 3-necked 250 ml flask, mounted over a magnetic stirring base, were placed 9-bromofluorene (2.45 g, 0.01 mol), $\text{Co}^{\text{II}}\text{Cl}_2$ (0.130 g, 0.001 mol) and dry THF (50 ml). To this was added a solution of benzyl magnesium chloride prepared from benzyl chloride (0.023 mol) in 100 ml THF under nitrogen atmosphere. The reaction mixture was refluxed for 3 hr and worked up in the usual manner. Separation of products on a silica-gel column using petroleum ether (b.p. $60-80^\circ$) and petroleum ether (b.p. $60-80^\circ$)-benzene (50:50, v/v) as eluants yielded bibenzyl 2.33 g, 9-benzylfluorene (0.180 g, $\sim 7\%$) and 9,9'-bifluoranyl (1.05 g, $\sim 64\%$). The effective yield of bibenzyl in the Co^{II} catalyzed reaction, therefore, was $2.33 - 0.51 = 1.72$, $\sim 86\%$.

Reaction of Benzyl magnesium chloride with Benzhydryl chloride in the presence of $\text{Co}^{\text{II}}\text{Cl}_2$

The above reaction was repeated using benzhydryl chloride (2.02 g, 0.01 mol) as the halide instead of 9-bromofluorene under otherwise identical conditions. Separation of products on a silica-gel column as usual yielded bibenzyl, 2.14 g (the effective yield of bibenzyl formed in the reaction is, therefore,